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# REPLACEABILITY OF FIXED AMMONIUM IN CLAY MINERALS

by

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# INTRODUCTION

Many soils and clay minerals will retain added $NH_4$ and K in such a manner that replacement by other cations is difficult. This $NH_4$ and K is said to be fixed.

There has been considerable interest in the fixation and release of $NH_4$ and K in soils and clay minerals because the exchange reactions involved affect the availability of the cations to plants and microorganisms. That is, fixation and release have considerable practical importance from the standpoint of efficient fertilizer use and the proper interpretation of soil test results. Furthermore, it is generally assumed that the fixed $NH_4$ and K ions are located between the layers of micaceous minerals in positions that were formerly occupied by lattice K. Therefore, information about the processes of fixation and release contributes also to our knowledge regarding the nature and weathering of micaceous minerals.

The manifestations of cation fixation may have implications in unsuspected directions. For instance, it has been demonstrated that relatively small amounts of a fixable cation, when present in the solution phase, can interfere with, or prevent completely, the displacement of cations that are located between the layers of 2:1 lattice type phyllosilicates. This interference with free exchange has been referred to as "blocking" or "trapping", depending upon whether the interlayer cations were themselves fixable or non-fixable, respectively. In

either event, this effect raises questions regarding the results obtained in many exchange studies, especially determinations of exchange capacity using $NH_4$ salts, studies of relative adsorption of cations on soils and clays where the salts used may not only have been impure but probably varied considerably in this respect, and in investigations into the kinetics of ion exchange where fixable cation levels were not kept below critical concentrations. Likewise, the conclusions drawn from studies of the availability of fixed $NH_4$ and K to plants and microorganisms will need to be re-evaluated.

Most of the work on cation fixation has been carried out with K. There are certain types of studies, however, in which $NH_4$ can be used to advantage. On the other hand, it is difficult to work with $NH_4$ in soils or micaceous minerals containing organic matter. Recent progress in the development of methods that will permit the separation of inorganic $NH_4$-N from soils without errors due to the breakdown of organic matter has stimulated renewed interest in the behaviour of $NH_4$ in soils. Nevertheless, to study the principles involved in the fixation and release of $NH_4$, there is still considerable information that can be obtained from the use of relatively pure clay minerals from natural deposits.

The present studies were initiated to investigate, by means of varied extraction techniques, the fixation and release of $NH_4$ by representative di- and trioctahedral minerals. Several reference clay minerals which were naturally low in

organic matter and which were treated, when necessary, to remove native interlayer K, were used in this investigation to determine the effect of various mineral characteristics upon $NH_4$ fixation.

# LITERATURE REVIEW

There are several recent reviews of the literature on the fixation and release of K and $NH_4$ (Barshad, 1955; Hanway, 1954; Leggett, 1958; Reitemeier, 1951; Schuffelen and van der Marel, 1955; Welch, 1958). Therefore the emphasis in the present compendium will be upon recently published material in those areas which are pertinent to the present study.

## Minerals Capable of Fixation

$NH_4$ fixation has been shown to occur in large but variable amounts in vermiculite (Barshad, 1948; Gruner, 1939), in very small amounts in illites from natural deposits (Allison and Roller, 1955) and in moderate amounts in montmorillonites (Allison and Roller, 1955; Joffe and Levine, 1947; Page and Baver, 1940). The much greater fixing abilities and lower K contents of the colloid fractions of illitic soils led Allison and Roller (1955) to the conclusion that, in general, the hydrous micas are more weathered or degraded in soils than in relatively pure reference samples from shales and underclays. The literature contains many reports of both $NH_4$ and K fixation in soils with particles of colloidal size identified as being montmorillonite (Allison, Kefauver and Roller, 1953; Stanford and Pierre, 1946; Truog and Jones, 1938). However, the possible presence of fixing minerals in the silt and sand size fractions of the soils studied was not discussed. That the coarser

materials may be important has been demonstrated by Barshad (1951). In a Swedish soil showing high fixing capacity studied recently by Nommik (1957), large amounts of vermiculite were present in the coarser fractions, whereas montmorillonite predominated in the colloidal size range. Stanford (1947) found that oven drying after saturation was necessary for K and $NH_4$ fixation by Wyoming bentonite, whereas Wear and White (1951) found that K was fixed but $NH_4$ was not under the same conditions. The ability of micaceous minerals to fix applied $NH_4$ and K is related to the degree of K removal or degradation of the mineral. Scott, Hunziker and Hanway (1960) showed an increase in $NH_4$ fixation by illite occurred when K was removed by degradation with sodium tetraphenylboron.

The general picture therefore appears to be that vermiculite and degraded illites will fix $NH_4$ readily in the moist state whereas montmorillonites must be dried. The amount of $NH_4$ fixed by montmorillonite is small, however, unless the $NH_4$-saturated material is dried at elevated temperatures. Hanway, Scott and Stanford (1957) found considerable amounts of $NH_4$ fixed in Wyoming bentonite that was heated in the ammonium state for 24 hours at 300-350°C.

## Mechanism of Fixation

Just as there are only certain clays capable of fixing cations on interlayer exchange sites, so are there also only certain cations which can be fixed on these clays. The

properties of the clays as well as the characteristics of the cations must therefore be considered in a discussion of the mechanism of cation fixation in clay minerals.

When K or $NH_4$ is fixed between the layers of micaceous minerals, expanding lattice clays of the 2:1 type are changed into minerals that do not show expansion upon hydration or glycolation. The mechanism which best explains the phenomenon is that suggested by Page and Baver (1940). They proposed that fixation occurs as a result of trapping of cations in the cavities formed by adjacent hexagonal oxygen rings of the silica sheets of two superimposed layers of a 2:1 type mineral. The cavities, having a radius of about 1.35Å, allow cations with the same, or slightly larger, radius to become partially embedded in the oxygen sheets without actual penetration into the lattice through either sheet. They showed that cations such as K, $NH_4$, Rb, Cs and Ba, with effective radii near that of an oxygen ring, were fixed by Wyoming bentonite and the colloid from Miami silt loam, which they called bentonite but which Allison, Kefauver and Roller (1953) identify as illite. Cations with larger or smaller unhydrated radii were not fixed. Page and Baver (1940) postulated that, if the attraction of a fixable cation to the adjacent sheets was sufficiently great, contraction, with exclusion of all or most of the interlayer water normally associated with expanded lattice minerals, could take place even under moist conditions. Drying, on the other hand, may be necessary for fixation of some hydrated ions of

suitable unhydrated size, or for the effective fixation of any ions by a clay whose bonding strength for interlayer cations is weak for reasons to be considered later. The implication is that, where fixation occurs, the adjacent sheets of the clay are bonded together so closely by the interlayer cations that movement of an ion from one void to the next is unlikely and escape from the clay virtually impossible. That is, a rather stable structure is formed requiring re-expansion of the plates before exchange can take place.

Wear and White (1951) emphasized that the location of the charge resulting from isomorphous substitution in the clay lattice has a direct bearing upon the fixing ability of a mineral. They suggest a bond length of 2.19Å for the K ion where the substitution is Al for Si in the tetrahedral sheets, and 4.99Å when the negative sites arise from substitution in the octahedral layer. The attractive force exerted on interlayer K would therefore be more than four times as great in the case of tetrahedral substitution. The well crystallized potassium mica, muscovite, with 25 percent substitution of Al for Si in the tetrahedral layer, represents the optimum in conditions favouring the retention of K in interlayer positions. Illite and vermiculite also have a relatively high degree of tetrahedral substitution, but less than the micas. Montmorillonite, on the other hand, has most of its charge arising in the octahedral layer. Wear and White (1951) found a direct positive correlation between the amount of K fixed and the proportion of the

net negative charge originating in the tetrahedral position in the four clay minerals which they investigated.

Barshad (1954b) places major emphasis upon the number of charges per unit volume, or the charge density of the mineral, rather than on the location of the charge. However, he arrived at this conclusion from a study of $NH_4$ and K fixation in a number of vermiculite samples that contained varying amounts of biotite and chlorite. The lower fixation on a weight basis in the vermiculite-chlorite materials could be due to dilution by the inactive fraction, rather than differences in charge density of the fixing portions. Barshad (1954b) went so far as to relate total interlayer charge to the level of fixation possible in a material. Nevertheless, it does seem logical that both charge density and the location of the charge should be important in determining the ease of replacement of an interlayer cation since they would both contribute to the force holding adjacent sheets together.

Since the present study is concerned with the replacement of fixed cations, the stability of a mineral undergoing this exchange of cations is important. Apparently the nature of the isomorphous substitution leading to the net negative charge on a clay mineral as well as the locale of this substitution are factors in determining stability. Barshad (1955) has discussed the implications of the stresses produced by larger $Al^{3+}$ proxying for smaller $Si^{4+}$ in fourfold coordination with oxygen in the silica sheets. He concluded that, while K leaves the micas

first, the Al is next, followed eventually by disintegration into silica tetrahedra and alumina octahedra. It is significant that no greater substitution of Al for Si in the tetrahedral layer than the 25 percent found in muscovite has been reported, suggesting that the stresses set up beyond this point could lead to instability.

The number and the valence of the cations present in octahedral positions also appear to have a bearing on the stability of the phyllosilicates. The clay minerals have been divided into two groups on the basis of the number of octahedral holes occupied. Using the terminology employed by Grim (1953) those with all of the octahedral holes occupied are called octaphyllites or trioctahedral, whereas those with two thirds of the possible positions filled are termed heptaphyllites or dioctahedral. Although other properties of clays within a group appear to grade continuously from one member to the next, the deviations from the di- and trioctahedral conditions are apparently not large. Grim (1953) gives the range for the 6 octahedral positions occupied as 4.00 to 4.44 in the dioctahedral and 5.75 to 6.00 in the trioctahedral minerals. Unfortunately, the use of this criterion in explaining differences between the behaviour of groups of clays does not appear to have much validity. Vermiculites, once considered to be largely trioctahedral, are mainly dioctahedral in soils, according to Jackson (1959). Although most illites described in the literature are dioctahedral, Grim (1953) makes reference

to reports on trioctahedral types. Montmorillonite is a dioctahedral member of the montmorillonite group which includes other di- and several trioctahedral minerals.

According to Barshad (1955), $Mg^{2+}$ and $Fe^{3+}$ should fit into the octahedral holes in the clay lattice without distortion. $Al^{3+}$ and $Fe^{2+}$ on the other hand are too small and too large respectively for the ideal radius ratio for a 6 fold coordination with O in the mica type of octahedron. Trioctahedral talc, $[2(Si_2O_5)]^{4-}\ [Mg_3(OH)_2]^{4+}$, has been classed as more resistant to acid attack than pyrophyllite, $[2(Si_2O_5)]^{4-}\ [Al_2(OH)_2]^{4+}$, with the basic dioctahedral structure of montmorillonite. However, in addition to size considerations, clay minerals with $Fe^{2+}$ in octahedral positions are likely to show added instability due to oxidation of the $Fe^{2+}$ to the trivalent state, which necessitates either the dropping of an interlayer cation or internal substitution to restore electrical neutrality. Biotite and muscovite are similar in having a high degree of tetrahedral substitution and stability resulting from the fourteen fold coordination of K in interlayer positions discussed by Wear and White (1951). However, the two minerals show marked differences in resistance to weathering as indicated by rate of release of K and the degree of clay breakdown by H-resins in studies such as those by Arnold (1958) and Stålhlberg (1959). Muscovite, the much more resistant of the two, is dioctahedral with Al in the octahedral sheet and little or no isomorphous substitution in the octahedral. Biotite is trioctahedral with

$Mg^{2+}$ and $Fe^{2+}$ usually occupying the bulk of the octahedral holes and again with little or no charge arising from the octahedral layer. Barshad (1955) attributes part of the relative stability of muscovite to somewhat closer packing of the crystal ($4.59\text{Å}^{03}$ compared to $4.89\text{Å}^{03}$ for the unit cell of biotite), but mainly to the divalent iron in the biotite. There is therefore nothing inherently less stable about the trioctahedral arrangement, but the octahedral cations can make trioctahedral minerals relatively easy to alter.

The effect of particle size on exchange properties and fixation has been studied to some extent. Layer silicates which have no inherent charge, or are non-expanding, depend upon broken bonds at the edges of the particles for their exchange capacity. Grinding such materials should result in an increase in the number of exchange sites, and Mortland and Erickson (1956) found this to be the case when pyrophyllite, kaolinite and illite were subjected to limited ball-milling. Jackson and Truog (1940), on the other hand, found that fine grinding, to near molecular size as they described it, destroyed the capacity of clay minerals to fix $NH_4$ and K against acetate extraction. However, the exchange capacities of the residues from the layer silicates (bentonite, nontronite, muscovite and a variety of soil colloids) were increased in all cases. Barshad (1954b) studied the effect of grinding on relatively pure vermiculites and mixtures of this mineral with chlorite and biotite singly and in combination. Reduction in size from

the original 2-10 mm diameter range to <0.1 mm resulted in slight increases in the amount of $NH_4$ absorbed in all cases, but proportionately large increases in the amount of $NH_4$ extracted by a KOH distillation. That is, the fixing capacity was reduced by limited grinding.

A similar effect of particle size on the level of $NH_4$ fixation was observed by Barshad (1951) in samples from a Sweeney subsoil, in which the 100-250 micron fraction fixed more $NH_4$ than did the <1 micron fraction. Kardos (1955) suggests that perhaps the failure to consider coarser soil fractions could explain some of the high fixation valves, and the somewhat contradictory evidence regarding fixation, in soils that supposedly contain only montmorillonite colloids.

The importance of ionic size in the fixation picture has already been discussed. Ionic valence and hydration are also factors which must be considered. Page and Baver (1940) reported some fixation, in the Miami soil colloid, of divalent Mg, Sr and Ba, but Ba was the only one held with anything approaching the tenacity shown by monovalent $NH_4$, K, Rb and Cs. The effective radius of the Ba ion falls between those of $NH_4$ and K. Since Ba was less tightly bound than either $NH_4$ or K, for a given ionic radius an increase in valency apparently reduces fixation. Barshad (1952) observed similar effects with vermiculite and bentonite and attributed them to the greater distance between the divalent ions and the site of the negative charge in the clay lattice. In a previous study Barshad (1950) related

the degree of hydration of bentonite and vermiculite, as reflected in the interlayer spacings, to the valence and on size of the cation, and to the charge density of the mineral. Small ions and divalent ions leave more room for water between the sheets, leading to a greater expansion of the lattice. The greater interlayer spacing and water content of air-dry bentonite compared to vermiculite saturated with the same cation he attributed to the difference in charge density between the two minerals. However, as pointed out previously, vermiculite not only has a higher charge density than bentonite, but a greater proportion of the substitution producing this charge resides in the tetrahedral layer.

Barshad (1950) considered K- vermiculite to have no water between the layers even in the air dry state, but concluded that a monolayer of water was present between the plates where $NH_4$ was adsorbed because of the slightly greater interlayer spacing. Hendricks, Nelson and Alexander (1940) concluded from careful dehydration studies that Na, K, H and trivalent ions are not hydrated when adsorbed by clay minerals, but divalent Ca and Mg have 6 molecules of water of hydration and monovalent Li, 3 molecules. Walker (1949) working with natural Mg-vermiculite, considered the Mg ions to be surrounded by 6 molecules of water in an octahedral arrangement when the clay was air dried. The water lost at 110°C, he believed, came from the unbound interlayer $H_2O$. The lattice spacings after oven drying suggested a monolayer of water between the plates, which he explained on

the basis of a redistribution of the 6 molecules of water of hydration of the Mg ion from an otahedral to a planar arrangement. The rapid rehydration of the 110° dried Mg vermiculite at room temperature he attributed to the strong tendency of the water of hydration to resume the octahedral arrangement. Complete dehydration of the Mg vermiculite reduced the C-axis dimension to 9.26Å , which is less than that of the well crystallized K micas.

The differential thermal curves for $NH_4$, K, Rb and Cs vermiculites obtained by Barshad (1948) do not show the low temperature endothermic peaks due to interlayer water which are strong for the same vermiculites saturated with Mg, Ca, Ba, Li or Na. Scott, Hanway and Stanford (1956) heated both $NH_4$- and K-bentonites and $NH_4$-vermiculite, and found the strong endothermic peaks between 100°C and 200°C with bentonite, but not with vermiculite. On the other hand, an $NH_4$-bentonite preheated at 350°C for 24 hours but subsequently re-hydrated, did not show loss of water at the low temperature but exhibited a pronounced exothermic peak at 550°C, which the authors attributed to volatilization of $NH_3$. They concluded that water was associated with the exchangeable $NH_4$ but not with the fixed.

It would appear from the foregoing that the hydration characteristics of ions in the solution phase are subject to change once the ion becomes absorbed, and dehydration and lattice contraction can lead to cation fixation even in the presence of excess water and at ordinary temperatures. As Kardos

(1955) states, there is much work needed in connection with the hydration of charged ions in the interlayer region.

## Factors Affecting $NH_4$ Adsorption

McBeth (1917) in his comprehensive study of $NH_4$ fixation, reported that Al, Fe and K salts added to soils prior to the addition of $NH_4$, markedly reduced the fixing power of the soil, whereas prior additions of Ca, Mg and Na salts had little effect. He also noted that the anion associated with a given cation had no effect on the results. The intereference of one fixable cation with the fixation of a second has subsequently been well established for soils, soil clays and clay minerals (Allison, Doetsch and Roller, 1951; Barshad, 1951; Nommik, 1957; Stanford and Pierre, 1946). In addition to K, Nommik (1957) found that Rb, Ba and La interefered with $NH_4$ fixation, although only Rb had a marked effect. He also confirmed McBeth's (1917) observations with respect to the lack of influence of Na, Mg and Ca.

Stanford (1947) concluded from his studies with electrodialyzed illite and acid washed bentonite that, in acid soils, H, Al and Fe, which he classed as difficultly exchangeable ions, must be removed before K can be fixed. Rich (1960) reported that $NH_4$ fixation by vermiculite was greatly reduced by the presence of a small amount of interlayer Al. With Al present, there was a marked increase in the stability of the vermiculite to heat treatment, and a decrease in the ability of the clay to expand.

Previous additions of acids to clays have resulted in a marked decrease in the fixation of $NH_4$ added thereafter, according to Attoe (1947), Barshad (1954a) and Wiklander (1950). Barshad (1954a) reported that exchangeable H was very difficult to remove from vermiculite with neutral salts, but boiling in neutral $Ba(Ac)_2$, or the addition of $Ba(OH)_2$ resulted in complete displacement. He noted little change in the capacity of vermiculite to retain $NH_4$ after being in the H state. Barshad (1954b) contributed the decreased fixation of $NH_4$ in acidified vermiculite to the somewhat expanded state in which the H leaves the clay lattice. However, an expanded condition should make the replacement of $NH_4$ easier than he reported in the previous paper. Whether or not H exchange should be considered as being similar to that of other cations is open to question. Barshad (1955) states that the exchange of cations such as Na, Ca, K and Mg requires only a slight alteration of the clay lattice in order to accomodate a replacing cation, whereas the adsorption of H brings about a disintegration of the lattice. Amphlett (1958) classified H exchange and cation fixation as two separate types of irreversible exchange, and states that it is impossible to replace all of the exchangeable H in a clay without partially destroying the structure by leaching out Al from the clay lattice into the interlayer spaces.

It is evident even from the limited amount of literature reviewed that acid clays fix little or no $NH_4$. Walsh and Cullinan (1945) consider K and $NH_4$ fixation to be particularly

associated with limestone-derived soils. There is considerable evidence that raising the pH of soils and clays does indeed result in an increase in fixation. Volk (1934) showed that while treatment of a soil with HCl decreased its K fixing power, application of $Na_2CO_3$ or $Ca(OH)_2$ increased fixation. Stanford (1947) increased both the moist and dry fixation of K in electrodialyzed illite by increasing the pH of clay suspensions with sodium or calcium hydroxide. Barshad (1954a) showed that the adsorption of $NH_4$, Na and Ba by partially H- saturated vermiculites was considerably less from neutral than from alkaline solutions. In the same study, by neutralizing the exchangeable H on acid leached or naturally acid vermiculite, he was able to restore fully the capacity of the clays to adsorb cations.

The fact that surface soils normally fix less $NH_4$ than subsoils has been noted by Hanway and Scott (1956) and Nommik (1957). Allison, Kefauver and Roller (1953) attributed this difference to the probable presence, in the surface soils, of $NH_4$ and K that is already fixed and also to the interfering effect of organic matter. Page and Baver (1940) did show a decrease in K fixation due to the adsorption of large organic cations by bentonite and a soil colloid. Dhariwal and Stevenson (1958) also found that a higher proportion of added $NH_4$ was fixed by subsoils than by surface soils, and that the subsoils, prior to $NH_4$ additions, contained a higher absolute level of $NH_4$ already in the fixed state. Stevenson and Dhariwal (1959)

postulate fixation during early geologic time as a sourse of the $NH_4$ found in sub-surface materials.

It is possible that organic molecules and mineral compounds such as precipitates of Fe and Al can, by a clogging action, reduce both the exchange capacity and the fixing ability of expanding lattice minerals. Dion (1944) pointed out that $Fe_2O_3$ adsorbed on clay minerals can reduce the cation exchange capacity. Scott, Ahlrichs and Stanford (1957) showed that the precipitation of aluminum phosphate on bentonite decreased fixation of potassium.

It would also appear that low equilibration temperatures are less favourable for $NH_4$ fixation than are higher temperatures. McBeth (1917) showed increased fixation with increasing temperature over the range of 5°C to 100°c. Nommik, working with a vermiculitic soil, used moist incubations at 3°, 21° and 60°C and corroborated McBeths findings. In view of the variable results reported for the effect of temperature upon cation exchange in general, as discussed by Grim (1953), it would seem that both fixation and release of $NH_4$ and K as a function of temperature need to be investigated for the various fixing minerals individually.

## Factors Affecting Chemical Extraction of the $NH_4$ and K in Clay Minerals

As shown by Barshad (1951), fixed ions cannot be replaced by other fixable cations, but are replaced by those able to expand the lattice. Wiklander (1950) used radioactive $K^{42}$ to

establish that only about 5 percent of the fixed K equilibrated with K in the soil solution. This would indicate that the interlayer cations are indeed non-exchangeable, and that the equilibrium is largely a static one rather than a dynamic interchange between a highly selective exchanger and a solution phase. To investigate the effect of mixing small amounts of a fixable cation with high concentrations of a replacing cation, Hanway, Scott and Stanford (1957) added increments of KCl and $NH_4Cl$ either directly to the $NH_4$- saturated clays (air dry Montana vermiculite and 350°C heated Wyoming bentonite) or to the NaOH and NaCl solutions, prior to adding these extractants to the clay. They showed that small amounts of K were effective in reducing the efficiency of NaOH as an extractant of fixed $NH_4$ from vermiculite and bentonite. When K was present at levels in excess of 2 K ions per 100 Na ions, no fixed $NH_4$ was released from vermiculite. Similarly, the presence of $NH_4$ and K in boiling 1N NaCl interfered with removal of the fixed $NH_4$ in the two clays, and, at high fixable cation concentrations, release of $NH_4$ from the clays stopped completely. Less $NH_4$ than K was required to achieve a given degree of blocking. This the authors attributed to the preferential adsorption of $NH_4$ over K by the vermiculite studied. Higher ratios of fixable to extracting cations were required for the same blocking effect in the boiling NaCl solutions as compared to the NaOH distillations. The heated bentonite was affected less than the vermiculite by a given concentration of fixable cations in

solution.

The effect of wetting and drying, and of air drying versus drying at 70°C, upon K fixation in Hagerstown silt loam was studied in some detail by Volk (1934). The K became more difficult to remove as the drying temperature and the number of wetting-drying cycles were increased. Hanway and Scott (1957) showed that the level of exchangeable K in soils is affected by wetting and drying, so that the fixation and release of $NH_4$ in soils will be influenced by this phenomenon. Walsh and Murdock (1960) studied several brunizem soils differing in the amount of moist exchangeable potassium present, and found a decrease in $NH_4$ fixation under moist, frozen and oven-dry conditions as the exchangeable K values increased. The inference is that soils with higher K- supplying power will have more of the fixing sites occupied by K.

Although more work is needed before the causes of $NH_4$ and K fixation or release on drying can be understood, De Mumbrum and Hoover (1958) have discussed one possible mechanism. Working with illite and vermiculite singly and in mixtures they concluded that while illite alone is a "release" mineral on drying, and vermiculite a "fixing" mineral, the two together showed an increase in exchangeable K upon dehydration, reversion of K upon re-moistening and fixation of applied K.

## Native Fixed Ammonium

Since the work of Rodrigues (1954) on tropical soils of British Guiana containing micaceous minerals, there has been

renewed interest in devising procedures to extract inorganic $NH_4$-N in the presence of organic matter. Rodrigues used a mixture of HF and $H_2SO_4$ and recovered as much as 75 percent of the total N (by Kjeldahl) in subsoils without, he believed, any of this amount being derived from the organic fraction. Hanway and Scott (1956) compared Barshad's double distillation technique for determining fixed $NH_4$ with Rodrigues' HF extraction and obtained similar results with subsoils, but higher results with surface soils using the HF-$H_2SO_4$ mixture. They also found native fixed $NH_4$ to be present in the soils studied, and an increase in the proportion of the total N in this form with increasing depth below the surface. Leggett (1958) also found the Rodrigues technique to overestimate the native fixed ammonium levels in the soils he studied. Bremner and Harada (1959) showed that a mixture 1N HCl-1N HF effected quantitative release of fixed $NH_4$ from clay minerals, but no significant conversion of organically-bound nitrogen to $NH_4$-nitrogen. Bremner (1959) extended this investigation to soils, and found that, on the average, 5.6 and 21.5 percent of the N in surface and subsoils, respectively, was fixed $NH_4$. He also found the Rodrigues technique to give much higher values, and Barshad's double distillation technique much lower results.

Dhariwal and Stevenson (1958), using an HF technique which they devised for studying fixed $NH_4$ in soils, found a decrease in C/N ratios with depth, which they attributed to an increasing proportion of N as fixed $NH_4$. Stevenson and Dhariwal (1959)

after using their HF technique on a number of soils, concluded that the amount of native fixed $NH_4$ was related to the clay mineral type. Soils containing illite had more native fixed $NH_4$ than those with montmorillonite clays, and kaolinitic soils contained the least. The levels of fixed $NH_4$ which they determined ranged from as high as 5 percent of the N in the surface samples to as much as 60 percent of the N in subsoils. They also concluded from analysis of samples from plots cropped continuously for an extended period, that cropping decreased the amount fixed, but increased the proportion of the N present as fixed $NH_4$ in surface soils. In a further application of the HF techniques, Walsh and Murdock (1960) also found appreciable fixed $NH_4$ in Wisconsin soils, and confirmed that the HCl-HF mixtures do not extract N from soil organic matter.

### Availability of Fixed Ammonium to Plants and Microorganisms

Although the literature dealing with the availability of the $NH_4$ applied to soils contains rather variable results from different sources, some of the reasons for the lack of agreement should become apparent from an appraisal of the methods employed.

Bower (1950) determined the availability of ammonium in two alkaline soils, prepared in such a manner that they contained the cation in both the fixed and the exchangeable form. Nitrification stopped after 14 days, at which time 78 and 87 percent of the exchangeable but only 13 and 28 percent of the

fixed was nitrified in the respective soils. Barley plants grown on the same soils recovered about the same proportion of the fixed $NH_4$, and approximately the same percentage of the exchangeable, as was nitrified in the companion experiment.

Allison, Kefauver and Roller (1953) conducted incubation experiments with a number of $NH_4$-saturated soils that had been leached with $CaCl_2$ or KCl to remove the exchangeable ammonium. Nitrification of the remaining $NH_4$ ranged from 5 to 24 percent in the KCl leached soil after 2 months incubation. The recovery was lowest for soils containing vermiculite, highest for those containing montmorillionite, and intermediate for the illitic materials. Nitrification was greater when $CaCl_2$ was used as a leaching solution. Adding K before the $NH_4$ to satisfy the fixing capacities of the soils resulted in an increase in the availability of added $NH_4$ in all soils.

Working with $NH_4$-saturated vermiculites, Allison, Doetsch and Roller (1953) reported that the fixed $NH_4$ was nearly as available to nitrifying bacteria as was $(NH_4)_2SO_4$. However, one vermiculite sample gave much lower results. For 6 montmorillonites, the availability of the fixed $NH_4$ amounted to 37 percent where $CaCl_2$ was used as the extractant and 29 percent where KCl was used prior to $CaCl_2$ before incubation. In this latter study carried out by Allison and Roller (1955) KCl was present in the nutrient solution which was added to the soil inoculum.

Aomine and Higashi (1953a, b) studied the availability of

ammonium in soils and vermiculite to plants and nitrifying organisms. They found a decided difference between rice and wheat in ability to recover the fixed ammonium, but concluded that while exchangeable $NH_4$ is easily nitrified, the fixed portion is less available both to plants and microorganisms.

Jansson (1958) found that a constant amount of $NH_4$ (20 ppm.) was nitrified between the 15th and 30th days of incubation, in experiments on the same soil prepared with 2 levels of fixed $NH_4$. Both Nommik (1957) and Jansson (1958) estimated the availability of fixed ammonium nitrogen to heterotrophic soil microflora by supplying low nitrogen energy material in large amounts to create a deficiency of nitrogen for the proliferation of the heterotrophs. Nommik found considerable release of fixed $NH_4$ which he attributed to increased microbiological activity. He also noted that added K strongly inhibited the defixation of the $NH_4$. Jansson reached similar conclusions and made the additional observation that the use of the difference between the total $NH_4$ added and that removed by KCl leaching as a criterion for fixed $NH_4$ overestimated the fixation against microorganisms.

Evidence for the adverse effect of added K salts upon nitrification and plant uptake of applied $NH_4$ is present in most of the literature already cited. In view of the effect of low levels of K upon $NH_4$ release from clay minerals, the possibility exists that the K present in inoculum or nutrient solutions was enough, by itself, to cause reductions in the

availability of so-called fixed $NH_4$. Welch and Scott (1959) were able to prepare an active culture of nitrifying bacteria having a K level of only 0.4 ppm. The nitrification by these organisms of $NH_4$ as $(NH_4)_2SO_4$ was not affected by the presence of K in amounts ranging from 0.4 to 300 ppm. At low K levels the $NH_4$ in $NH_4$-saturated vermiculite (95% fixed) was as available as that in $(NH_4)_2SO_4$ but recovery dropped rapidly as the K level increased until at 300 ppm. only slightly more than the exchangeable $NH_4$ was nitrified. It was also found that the effect of a given quantity of adsorbed K on nitrification increased as the degree of $NH_4$ saturation decreased.

In the same study Welch and Scott (1959) found that recovery of the $NH_4$ in a bentonite dried at 350°C and in a slightly degraded illite dried at 110°C was never complete even in the absence of added K, although potassium additions did decrease the recovery of $NH_4$ as nitrate. Removing some of the fixed $NH_4$ from these clays resulted in a higher percentage of the $NH_4$ present remaining un-nitrified. Bentonite, when dried at 110°C instead of 350°, had little fixed against K-salt extraction and all of the $NH_4$ was available for nitrification. Removal of some of the K from illite prior to $NH_4$ saturation increased the amount of $NH_4$ absorbed by the clay and decreased the proportion available to the nitrifiers.

The implications of the above study with respect to the effect of K status of a soil in determining the recovery of fixed $NH_4$ by plant or by microorganisms are obvious. Recently Walsh

and Murdock (1960) reported a highly significant correlation between the moist exchangeable K present after cropping and the amount of applied $NH_4$ fixed against crop removal. Further studies along this line will no doubt be appearing in the near future. The inter-relationship between $NH_4$ and K fixation in soils demonstrated by Stanford and Pierre (1946) in the laboratory would appear to be operative under field conditions.

## Methods of Determining Exchangeable and Fixed Ammonium

It is apparent from the foregoing discussion that the term "fixed ammonium" used in the quantitative sense is strictly arbitrary. Barshad (1951) suggested that the difference between the ammonium removed by boiling in NaOH and that removed by boiling in KOH be considered as fixed. Stanford and Pierre (1946) used as the criterion for fixation that part of the added $NH_4$ not removed by leaching with N KCl. A total N determination by a Kjeldahl procedure, following saturation of the soil with $NH_4$ and KCl leaching to remove the exchangeable, was used by Nommik (1957). He also employed an $HF-H_2SO_4$ technique to dissolve the silicate minerals after first treating his soils with KCl, and the results obtained for fixed ammonium by Barshads technique, Kjeldahl digestion, and HF extraction were quite comparable. The use of HCl-HF mixtures as recommended by Dhariwal and Stevenson (1958) and Bremner (1959), following KOH and KCl pre-treatments respectively, minimize the interference from organic matter while extracting all of the $NH_4$

present in silicate minerals. Allison, Doetsch and Roller (1951) extracted with N KCl after adding $NH_4$ salts. The difference between the total N by Kjelkahl in these samples and the total N in control soils extracted with KCl but not treated with $NH_4$ salts, was used as an estimate of fixed ammonium. Leggett (1958) adopted an aeration-recovery technique involving a room temperature distillation using $K_2CO_3$ to remove the excess soluble and readily exchangeable ammonium.

There are certain advantages and disadvantages to all of the preceding methods from a practical standpoint, but it is not proposed to go into these in detail here since the use of any estimate of fixed ammonium, as presently conceived, is of questionable value. While it is important to have an accurate method of measuring the total inorganic $NH_4$-N present in soils, especially for studies involving N-containing organic compounds, the total present may bear no relationship to plant availability. Such is the case with other nutrient elements, K and P being good examples. Furthermore, an arbitrary subdivision of the total $NH_4$ into fixed and available portions does not improve the situation. It is obvious from the literature on biological availability that a considerable amount of the $NH_4$ not extracted by K salts or KOH is available to plants and microorganisms over a relatively short period of time. HF procedures may overestimate the total potential supply of $NH_4$ by bringing in native fixed $NH_4$, which, by its very presence in cropped soils is of necessity as unavailable as Walsh and

Murdock (1960) found it to be. An estimate of available $NH_4$ which is too low subtracted from a total which may be too high cannot produce a meaningful figure.

A more satisfactory method of extracting $NH_4$ for correlation with biological availability would be one regulated by the K-releasing power of the soil. However, in view of the difference in behaviour displayed by different fixing minerals and soils to accumulations of K in the extracting solutions, as illustrated by the work of Hanway, Scott and Stanford (1957) and Nommik (1957), the procedure should also show differential behaviour to the different minerals. Absence of attack upon organic constituents would also seem to be a necessary attribute of any method for determining the availability of inorganic $NH_4$-N. In short, good methods are needed for total exchangeable $NH_4$ and for biologically available $NH_4$. However, more information is needed on the factors affecting $NH_4$ release from soil minerals.

Falling somewhere in between the methods for determining total and K-exchangeable inorganic $NH_4$-N are a number of equilibration or leaching procedures using salt, acidified salt or acid solutions for routine determination of what is loosely termed the $NH_4$ in soils (Jackson, 1958; Metson, 1956; Piper, 1944). That some of these may be rather inefficient in view of K and $NH_4$ accumulations in solution has been demonstrated by Hanway (1954); Nommik (1957), and Scott, Hanway and Edwards (1958). For alkaline distillations likewise, even though $NH_4$

accumulations are not a factor, the possibility of K interference has been demonstrated by the same workers and by Allison and Roller (1955) and Hanway and Scott (1956). As pointed out by Bremner and Shaw (1955), direct boiling distillation techniques have been largely abandoned in $NH_4$ determinations not only because of K interference but due to decomposition of organic N compounds, and they suggested the use of a room temperature distillation using MgO in modified Conway microdiffusion cells. Recently, however, Bremner[1] has devised a rapid steam distillation technique using MgO which has produced no breakdown of a wide range of N containing compounds tested while permitting the removal of all of the $NH_4$ present. This type of distillation is considered to be more satisfactory than the borate buffer technique of Bremner and Shaw (1954).

Cation exchange resins have found application in connection with K removal from soils and minerals. Pratt (1951) found a correlation coefficient of 0.963 between K removed by cropping and that removed by H-Dowex-50 in a 2 month incubation, even though the resin removed an average of 4.85 times as much K as the crop of alfalfa. The best single criterion appeared to be the exchangeable K present in the soil before cropping, but including the non-exchangeable K removed by the resin increased the accuracy of the prediction of K removal by alfalfa.

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[1]Bremner, J. M. Ames, Iowa. Techniques for distillation of $NH_4$. Private communication. 1959.

Arnold (1958) found that Na-Amberlite IR-120 took up approximately the same amount of K from soils as was extractable by leaching with neutral N $NH_4OAc$. Ca-Amberlite extracted less, and H-Amberlite extracted considerably more than the $NH_4OAc$, and the K removed by the H-resin continued to increase over a period of a month or more. He found good agreement between the amount of K extracted by H-Amberlite and that which was available to crops on two long-term experimental sites having had no K added for periods of 50 and 100 years. The results which Arnold (1958) obtained with K bearing minerals are also interesting. He found the H-resin was capable of extracting non-exchangeable K but the removal of K by the resin was discriminatory in nature. Muscovite and hydrous mica (illite), known to release K very slowly to crops, were correspondingly resistant to H-resins. Biotite, on the other hand, was completely broken down within 10 days with the release of all of its potassium. In general, the dioctahedral minerals were resistant, the trioctahedral were readily altered. It was only with the trioctahedral biotite and the K-vermiculite that the Na- and Ca- resins were able to extract considerably more than the $NH_4OAc$ extractable K present. Salomon and Smith (1957), working with soils, found that the K removed by extraction with H-Amberlite IR-120 was a better index of the availability of this element to crops than buffered acetate extractions or a nitric acid method for non-exchangeable potassium.

Precipitants to keep the concentration of K in solution

low have been found useful in the degradation of K-bearing minerals. White (1951) used sodium cobaltinitrite to assist in the removal of K from illite, and found the lattice spacings characteristic of montmorillonite in his material after degradation. Scott, Hunziker and Hanway (1960) used a mixture of NaCl and $NaBPh_4$ (sodium tetraphenylboron) to remove K and increase the $NH_4$ fixing capacity of a specimen illite. They were able to increase the $NH_4$ on the illite from 20 me. to 36.2 me./100 g. and found that 11 of the extra 16.2 me. were fixed against KOH distillation.

Leggett (1958) attempted to use $NaBPh_4$ in his room temperature aeration-distillation $NH_4$ from soils. The recovery of $NH_4$ ($NH_4OAc$) that was added to the soil decreased, however, as the amount of added $NaBPh_4$ increased. The recovery of $NH_4$ was improved, however, at all levels of addition by saturating the soil with Na prior to the distillation. The addition of K as KCl to water solutions of $NH_4OAc$ and $NaBPh_4$ likewise decreased the recovery of ammonium. The author concluded that the solubility of $NH_4BPh_4$ was lowered in the presence of precipitated $KBPh_4$. However, since both compounds are stable at the pH of 0.7N $Na_2CO_3$, it would be expected that the distillation of $NH_4$ from its tetraphenylborate salt would be dictated by the solubility of $NH_4BPh_4$. Thus it would be slow because this compound is very insoluble.

Thermal studies of $NH_4$-saturated clays have been conducted in an attempt to relate the temperatures at which $NH_3$ is lost to

the energy of adsorption of the $NH_4$. Cornet (1943) concluded from just such a study that the adsorption site did determine the temperature at which $NH_4$ decomposed. He also determined the C-axis dimensions of $NH_4$-bentonite heated to 400°C and found a 9.8Å spacing, which was the same as that for a H-bentonite dried at 100°C. With only 7% of the $NH_4$ left, it appeared that a H-clay remained due to the decomposition of the $NH_4$. Scott, Hanway and Stanford (1956) investigated $NH_4$-saturated samples of Kaolonite, illite, bentonite and vermiculite. They found that fixed $NH_4$ ions appeared to resist thermal decomposition more than the exchangeable, but there was no sharp separation between the two. In the case of vermiculite there was no loss of $NH_3$ below a temperature of 375°C. By the time this temperature was reached practically all of the $NH_4$ had been removed from the illite and bentonite. This is in direct contrast to the relative availability of the $NH_4$ in these clays to nitrifying organisms as shown by Welch (1958).

# MATERIALS AND METHODS

## Clay Minerals

### Vermiculite

All of the vermiculite samples that were used in this study were prepared from a bulk sample of Montana vermiculite that was supplied by F.E. Allison, U.S. Department of Agriculture. Barshad (1948) classified material from the same source near Libby, Montana, as a relatively pure vermiculite mixed with interleaved vermiculite-biotite. Portions of the same bulk sample have previously been used by Allison. Roller and Doetsch (1952), Hanway (1954), Scott, Hanway and Edwards (1958), and Scott, Edwards and Bremner (1960).

In its original form the Montana vermiculite consisted of relatively large and thick flakes of vermiculite and vermiculite-biotite with small amounts of impurities that appeared to be chlorite, quartz and ferro-magnesian minerals upon casual inspection. The initial preparation consisted of grinding the vermiculite in a Christy and Norris laboratory hammer mill using a screen with round holes 1/16 inch in diameter. A few relatively large, thin flakes appeared to slip by without being crushed, therefore, the ground material was passed through a screen with holes 2 mm. in diameter either before or after subsequent $NH_4$ saturation but prior to use of the material in extraction studies. The size distribution of the ground vermiculite after having been sieved through a 2 mm. screen and as

determined by hand sieving sample 2A (table 1) is as follows:

| | | |
|---|---|---|
| >2 mm. . . . . | 0 | percent |
| 2 - 1 mm. . . . . | 1.2 | " |
| 1 - 0.5 mm. . . . . | 24.5 | " |
| 0.5 - 0.25 mm. . . . . | 48.0 | " |
| <0.25 mm. . . . . | 26.2 | " |

The procedure adopted for saturating the vermiculite with $NH_4$ consisted of leaching several hundred grams in a large Buchner funnel with N $NH_4Cl$ for 48 hours. Suction was used only to remove the last remaining portions of each addition of $NH_4Cl$ before applying fresh salt solution. The clay was subsequently washed with 70 percent ethanol until the leachate gave a negative test for $NH_4$ with Nessler reagent, or for chloride ions with $AgNO_3$. The material was then air-dried in a constant temperature room at 25°C and a relative humidity in the vicinity of 25-30 percent for a period of several days.

One ground vermiculite sample (3A) was subjected to degradation in a mixture of NaCl and $NaBPh_4$ before it was $NH_4$-saturated. The details of the degradation procedure used were similar to those described later in this section for illite.

Brief descriptions of the various vermiculite samples which were prepared and used at different stages of this study of $NH_4$ removal are given in table 1. There was no native N in these samples, therefore the only $NH_4$ present was that added as $NH_4Cl$.

Table 1. Montana vermiculite samples prepared for this study of $NH_4$ fixation and release

| Sample | Description | % moisture (110°C) | me. $NH_4$/100 g. oven-dry clay |
|---|---|---|---|
| 2A | < 2 mm., natural vermiculite, air dried, source of vermiculites 2B, 2C | - | 0.0 |
| 2B | < 2 mm., $NH_4$-saturated, air dried | 0.92 | 82.1 |
| 2C | < 0.25 mm., $NH_4$-saturated, portion of 2B ground in an agate mortar to pass a 60 mesh screen, air dried | 0.92 | 82.1 |
| 3A | < 2 mm., natural vermiculite, air dried, source of 3B and 3D | - | 0.0 |
| 3B | < 0.5 mm., $NH_4$-saturated, air dried, sieved after $NH_4$-saturation | 0.76 | 85.8 |
| 3C | > 0.5 < 1.0 mm., $NH_4$-saturated, the coarse material remaining from sieving for sample 3B, air dried | 1.69 | 85.4 |
| 3C' | > 0.1 < 0.25 mm., $NH_4$-saturated, sieved from a portion of 3C ground in an agate mortar, air dried | 2.09 | 83.4 |
| 3C'' | < 0.05 mm., $NH_4$-saturated, portion of 3C ground in an agate mortar to pass a 300 mesh screen, air dried | 2.21 | 82.5 |
| 3C''' | < 0.05 mm., $NH_4$-saturated, portion of 3C'' leached with $NH_4Cl$, air dried | 1.29 | 108.0 |
| 3D | < 0.5 mm., $NH_4$-saturated, portion of 3A, sieved and given a NaCl - $NaBPh_4$ degradation prior to $NH_4$-saturation, air dried | 1.86 | 157.7 |

Illite

The illite samples were derived from 2 bulk portions of Goose Lake Grundite, a Pennsylvanian underclay from near Morris, Grundy County, Illinois. Both shipments were obtained from the Illinois Clay Products Co., the first in 1952 and the second in 1959.

Samples prepared from the 1952 batch of Goose Lake Grundite were used previously by Hanway (1954), Hanway, Scott and Stanford (1957), Scott, Edwards and Bremner (1960), Scott, Hunziker and Hanway (1960) and Welch (1958). For the purposes of the present study samples originating from this batch of illite were neither fractionated nor treated to remove native nitrogen. These samples, did, however, receive a mild degradation treatment prior to $NH_4$ saturation.

The initial step in the preparation of all samples originating with the 1959 batch of Goose Lake Grundite was a heat treatment in a muffle at 450°C for a period of 24 hours to remove the N present. The illite was then Ca-saturated by mixing a thick suspension of the clay with enough Ca-saturated Amberlite IR-120 in water to give a ratio of exchange capacities which was approximately 8:1 in favor of the resin. The < 20 micron material was removed by repeated sedimentations of the coarse fractions from dilute suspensions of the clay in $NH_4$-free distilled water. The < 20 micron clay was subsequently separated from the water using an auto-irrigator as a filter, air dried and ground in an agate mortar to pass a 60 mesh screen.

The slightly degraded 1952 Goose Lake Grundite was $NH_4$-saturated by treating the illite with $NH_4$-saturated Amberlite IR-120 as described by Welch (1958). The undegraded, 450°C heated < 20 micron material from the 1959 Goose Lake Grundite was $NH_4$-saturated by the leaching technique employed with vermiculite. Both of these $NH_4$-saturated illite samples were then leached with 70% ethanol subsequent to $NH_4$ saturation until chloride free, dried for 24 hours at 105-110°C and ground in an agate mortar to pass a 60 mesh sieve. Both $NH_4$-saturated samples were then equilibrated at 25°C at approximately 35 percent relative humidity for a period of 48 hours.

The slight degradation of the 1952 Grundite samples already mentioned resulted from the treatment of 1000 g. of the clay with 1 liter of 4N NaCl that also contained $NaBPh_4$ and enough HCl to adjust the system to pH 5. After shaking for 72 hours, 230 g. of NaCl and 2 liters of acetone were added. This mixture was shaken for 2 hours to dissolve the $KBPh_4$ precipitate, and the clay filtered in an auto-irrigator. The filtered material was then air dried and ground to pass a 60 mesh sieve.

A more efficient procedure not requiring acetone was used in the degradation of the 1959 Grundite sample. An unbuffered mixture of N NaCl and $NaBPh_4$ (pH 9) was used and 10 changes of solution made over a period of 10 days. The clay suspension (170 g. in 1 liter) was stirred after each addition, allowed to settle for a period which varied from 2 hours at the start to about 3 days for the final treatment, and the $KBPh_4$, which

remained as a scum on the surface, was siphoned off along with part of the NaCl solution. Boiling the remaining NaCl-clay mixture after the first removal of precipitate usually brought more $KBPh_4$ to the surface. Fresh NaCl was added at intervals to keep the volume up for purposes of boiling and decantation or siphoning. After the last application of NaCl-$NaBPh_4$ had been siphoned off, successive dilutions with low K-solution of NaCl were used to reduce the $NaBPh_4$ concentration to a low level, and after boiling to break down completely any dissolved or precipitated tetraphenylboron, 1 N $NH_4Cl$ was added. The suspension was then filtered and leached for a total of 48 hours with more 1 N $NH_4Cl$. Thereafter they received the same treatments as the other $NH_4$-saturated illite samples.

The data on the illites are summarized in table 2.

Bentonite

All samples were prepared from the same batch of Wyoming (Volclay) bentonite mined from deposits of cretaceous age found in the Black Hills region of South Dakota and Wyoming. The raw material was supplied by the American Colloid Co. Samples prepared from this same material have been used in many studies, a few of the more recent published works being those of Hanway, Scott and Stanford (1957), Scott, Ahlrichs and Stanford (1957), and Scott, Edwards and Bremner (1960).

The No. 1 group of bentonites were prepared from the natural, largely Na-saturated Volclay material without pre-treatment.

Table 2. Illite samples prepared for $NH_4$ fixation and release investigations

| Sample | Description | % moisture (110°C) | Total N as me. $NH_4$/100 g. oven dry clay |
|---|---|---|---|
| 1A | 1952 Goose Lake Grundite, slightly degraded, no size fractionation or heat treatment | - | 6.1 |
| 1B | Portion of 1A $NH_4$-saturated using $NH_4$-saturated resin, 110°C dried | - | 31.4 |
| 2A | 1959 Goose Lake Grundite, heated 450°C for 24 hrs., <20 microns, undegraded, air dried | 4.10 | 0.0 |
| 2B | Portion of 2A $NH_4$-saturated by leaching with N $NH_4Cl$, 110°C dried | 1.64 | 27.0 |
| 2C | Portion of 2A degraded for 10 days in NaCl-$NaBPh_4$, then $NH_4$-saturated, 110°C dried | 2.00 | 71.6 |

All of these samples (1B, 1C and 1D) were $NH_4$-saturated by leaching for 48 hours with N $NH_4Cl$, followed by alcohol washing to remove chlorides. Sample 1B was subsequently oven-dried at 110°C for 24 hours, then ground to pass a 60-mesh sieve before being re-exposed to an atmosphere of approximately 30 percent relative humidity at a temperature of 25°C. Samples 1C and 1D were heated in different muffle furnaces at 350° for 24 hours in the $NH_4$-saturated state and were subsequently treated like 1B.

The No. 2 and 3 bentonite groups originated from a single bulk sample 2A that was prepared by subjecting the natural Volclay bentonite to the following pre-treatments, applied in the order given:

1. A 24 hour heat treatment in a muffle furnace at 450°C to remove organic materials (total N content of the natural bentonite was equivalent to 1.1 me. $NH_4$ per 100 g. clay).
2. Suspension in a large volume of distilled water to dissolve the soluble salts, which were then removed by filtering in an auto-irrigator.
3. Treatment with Ca-saturated Amberlite IR-120 using a ratio of exchange sites on the resin to those on the clay of approximately 9 to 1.
4. Separation of the $<2$ micron size fraction from a 1 percent suspension by repeated sedimentations of the coarser material and withdrawal of the supernatant liquid.
5. Concentration of the $<2$ micron clay by removing the water by filtering in an auto-irrigator.
6. Drying at room temperature for several days followed by crushing in an agate mortar to pass a 60 mesh screen.

Saturation with $NH_4$ to obtain samples 2B and 2C was accomplished by repeated washings with $\underline{N}$ $NH_4Cl$ in centrifuge tubes, followed by alcohol washing, air drying and grinding to pass a 60 mesh sieve. Sample 2B was dried in an $NH_4$-saturated

state for 24 hours at 110°C, whereas 2C was heated in a muffle at 350°C for the same period.

Samples 3B and 3C are $NH_4$-saturated bentonites that were heated at 110° and 350° respectively. They were $NH_4$-saturated in the same manner as samples 2B and 2C, but after having been subjected to a treatment with NaCl-$NaBPh_4$ similar to that given the 450° heated illite. Total K determinations on bentonites 2B, 2C, 3B and 3C showed, however, that they all contained 0.48 me. K per 100 g. of oven dry clay. The degradation therefore had no effect on the amount of K present, suggesting it may be present in the $<2$ micron material in some mineral other than a layer silicate.

The bentonites used in studies of the release of $NH_4$ are listed in table 3.

## Analytical Procedures

Considerable attention was paid to the choice of a Kjeldahl procedure since preliminary work indicated that total N determinations on certain clays required long digestion times for maximum recovery. The procedure finally developed and used throughout the present work was based upon recent unpublished work by Bremner[1]. The details of the digestion are as follows: 0.1-0.5 g. samples of clay (maximum $NH_4$ content approximately

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[1]Bremner, J.M. Ames, Iowa. Details of efficient Kjeldahl procedures. Private communication. 1957.

Table 3. Bentonite samples prepared for $NH_4$ fixation and release investigations

| Sample | Description | % moisture | Total N as me. $NH_4$/100 g. oven dry clay |
|---|---|---|---|
| 1B | No pre-treatment, $NH_4$-saturated by leaching, 110°C dried | - | 76.8 |
| 1C | As for 1B, but heated at 350°C for 24 hours in the $NH_4$ state | - | 20.5 |
| 1D | As for 1C, but heated in different muffle | 0.41 | 50.4 |
| 2A | 450°C heated, Ca-resin treated, < 2 micron clay, air dried | - | 0.0 |
| 2B | $NH_4$-saturated portion of 2A, 110°C dried | 6.2 | 82.6 |
| 2C | As 2B, but heated at 350°C for 24 hours in $NH_4$ state | 0.9 | 41.5 |
| 3B | "Degraded" equivalent of 2B | 4.8 | 79.7 |
| 3C | "Degraded" equivalent of 2C | 0.8 | 35.9 |

0.2 me.) were weighed into dry semi-micro Kjeldahl flasks (100 ml., bulb type); 2 ml. $H_2O$ were added and the clays allowed to stand in the moist state for about 20 minutes prior to the addition of $H_2SO_4$ to speed up the rate of breakdown of the clay by the acid; 10 ml. of concentrated $H_2SO_4$ were added next, and the mixture digested for about 1 hour or until all of the water had been boiled away; 3.0 g. of a mixture made up of 100 parts

$K_2SO_4$, 10 parts of $CuSO_4 5H_2O$ (dried and ground previously) and 1 part powdered Se. or, 3.4 g. of a similar mixture where an equivalent amount of $Na_2SO_4$ had been substituted for the $K_2SO_4$, was added through a glass funnel; digestion was continued for a minimum of 6 hours, with frequent mixing of the contents of the flask. For the resistant clays e.g. 350° heated $NH_4$ bentonite, an 18 hour heating period was required; approximately 2 hours before termination of the digestion an additional 5 ml. acid was added to wash down any clay on the sides of the flask.

Digestion was carried out on an Aminco semi-micro digestion rack with adjustments for varying the level of the flask above the electrical resistance wires for heat control, and with shielding to protect the necks of the flasks from direct heating. The maximum temperature possible with this heating unit is 350°C, which is slightly above the boiling point of the acid-catalyst mixture used.

Distillation was accomplished from large (800 ml.) short-necked Kjeldahl flasks, after repeated washings were made to transfer the material from the digestion flasks. Heating in the presence of dilute acid was sometimes required to free all of the digest from the sides of the small digestion flasks. An excess of 10 N NaOH (reagent grade) was added, based upon the total equivalents of acid used in the controls, and approximately 225 ml. of distillate collected in 25 ml. saturated boric acid over a period of 0.5 hours. The distillation rate was adjusted to keep the temperature of the condensate in the collecting

flask at, or below, room temperature. An indicator mixture containing equal parts of 0.2 percent methyl red and 0.1 percent methylene blue, both in 95 per cent ethanol, was used in the titration of the $NH_4$ with 0.01 N HCl. At least 1 blank was carried along with each series of samples and this was titrated first, so that the samples could be brought to the same end point.

A similar procedure was used for distillation of the $NH_4$ removed from the clays by the various extraction techniques employed e.g. by salts, resins or dilute acids. After the clay was removed by filtering or centrifuging, the extracting solution plus leachate was made up to about 350-400 ml., and approximately 30 mls. of 40 percent base added. Whenever there was the possibility that some finely divided colloidal clay remained in the filtrate or supernatant, KOH rather than NaOH was used as the alkali in order to collapse the clay lattice and prevent the displacement of $NH_4$ from the clay during the actual distillation.

A semi-micro steam distillation procedure was also used in connection with studies on the removal of $NH_4$ from clays by solutions containing $NaBPh_4$. The apparatus used was designed by Bremner[1] for the conversion of various forms of soil N to $NH_3$ by short-term steam distillations using MgO as a base. As

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[1]Bremner, J.M. Ames, Iowa. Distillation equipment for $NH_4$ determinations. Private communication. 1959.

employed in the present study, $NH_4$ was distilled directly from clay-water or clay-water-acetone mixtures using MgO or NaOH and the distillate was collected in boric acid. Distillation times of 4 minutes and a volume of distillate in the vicinity of 30 ml. were required to obtain complete recovery of the $NH_4$ in solution.

Direct room temperature distillations of $NH_4$ were made from alkaline systems using the modified Conway microdiffusion cells described by Bremner and Shaw (1955), the $NH_3$ absorbed in the centre well being titrated with 0.005 N $H_2SO_4$ from a 2 ml. micro-burette.

Total K was determined using the HF-$HClO_4$ digestion procedure described by Jackson (1958), followed by a quantitative determination of the K in solution with a Perkin-Elmer model 52-C flame photometer and Li as the internal standard.

When it became apparent early in the work with resins that small amounts of $NH_4$ were present in the condensed steam used as distilled water, the practice was adopted of passing this water through resin columns packed with H-saturated Amberlite IR-120 before it was used in any phase of the $NH_4$ extraction work.

The Na and Ca salts and bases used in this study were selected for low K content. The reagent grade NaCl, for instance contained $< 0.000$ percent K.

# REPLACEABILITY OF AMMONIUM IN MONTANA VERMINULITE

## K Blocking

The replaceability of ammonium in Montana vermiculite by boiling alkali and salt extractions was investigated by Hanway, Scott and Stanford (1957). The study was continued with neutral and acidified salt and acid solutions by Scott, Hanway and Edwards (1958). In this work it was noted that the efficiency of boiling NaOH distillations, ordinarily capable of removing all of the $NH_4$ from vermiculite in 1 to 2 hours, was sharply reduced by the presence of small amounts of K in solution. The addition of 2 K ions per 100 Na ions was sufficient to lower the amount of $NH_4$ removed by NaOH to a level not far above the value for a comparable KOH distillation. In neutral and acid salt extractions both $NH_4$ and K blocked the release of the $NH_4$ in the vermiculite.

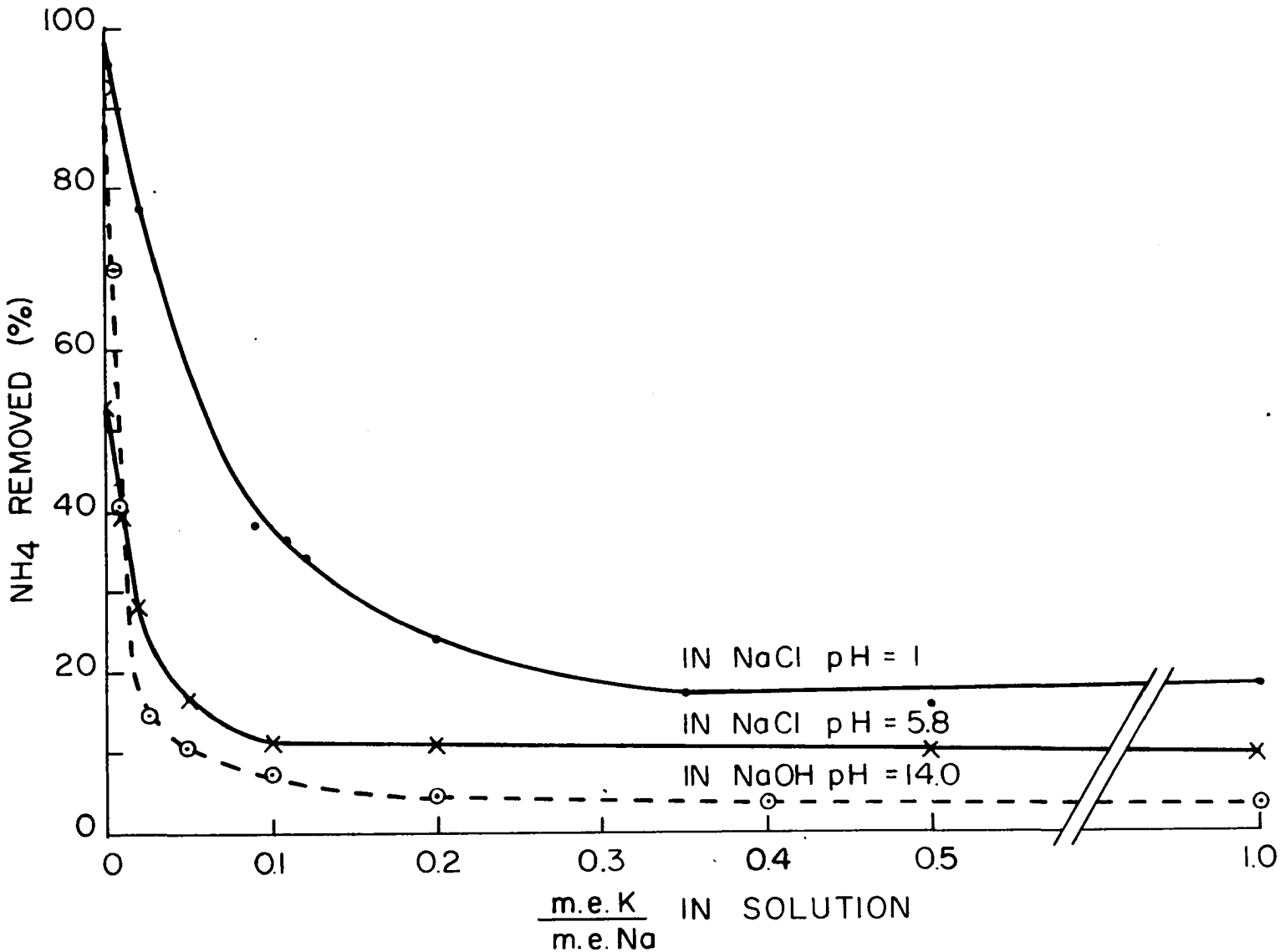
In the later study, the blocking effect of replaced $NH_4$ that accumulated in neutral and acid salt extractants was demonstrated by the fact that several successive extractions of a clay sample with fresh solution removed more $NH_4$ than a continuous extraction for the same total time of contact. Also, the blocking effect of a given ratio of $NH_4$ to Na upon further exchange of $NH_4$ was found to decrease with decreasing initial pH of the salt solution used as extractant. Hanway, Scott and Stanford (1957) had also reported that higher K to Na ratios were required in neutral salt treatments than in alkaline

distillations to produce the same degree of blocking. The relationship between the blocking effects of K and $NH_4$ and the pH of the extracting solution over a wider range of conditions was therefore investigated.

In order to ascertain whether or not the blocking effect of added K was a continuous function of pH over the range from 1 to 14, 1 g. samples of vermiculite 2B were boiled for 1 hour in 100 ml. of 1 N NaCl(pH 5.8), 1 N NaCl-0.1 N HCl(pH 1) and 1 N NaOH(pH 14). The three solutions were prepared with increments of added K (KCl) ranging from 0 to 100 me. per 100 ml. To minimize changes in concentration and to avoid loss of $NH_3$ in the salt extractions, the sample flasks were fitted with reflux condensers of small bore. In the case of the NaOH distillations, $NH_4$-free distilled water was added continuously through separatory funnels at the same rate as the distillate was collected in the receiving flasks. The effect of the various K levels on the percentage of $NH_4$ removed from the vermiculite in 1 hour by the three extractants is shown in figure 1. The total $NH_4$ in vermiculite 2B by Kjeldahl analysis was 82.1 me. per 100 g.

With no K added the 1 hour NaOH distillation removed practically all of the $NH_4$ present. Hanway, Scott and Stanford (1957) explained the effectiveness of NaOH in the absence of added K as being due to the fact that the replaced $NH_4$ is continually volatilized off as $NH_3$ in the alkaline system. A 1 hour digestion in the near-neutral 1 N NaCl, on the other hand,

Figure 1. $NH_4$ removed by boiling 1 g. of $NH_4$-saturated vermiculite 2B for 1 hour in 100 ml. of 1 N Na solutions as influenced by pH and the amount of added K.


100
80
60
40
20
0
NH4 REMOVED (%)
IN NaCl pH = 1
IN NaCl pH = 5.8
IN NaOH pH = 14.0
0
0.1
0.2
0.3
0.4
0.5
1.0
m.e. K / m.e. Na IN SOLUTION

removed only about 50 percent of the $NH_4$ present because the replaced $NH_4$ which accumulated in solution blocked further displacement. The NaCl-HCl solution at pH 1, however, removed nearly as much $NH_4$ as NaOH in spite of the greater concentration of $NH_4$ in the acid solution. This reduction in the blocking effect of $NH_4$ was due to the acid conditions and it has been attributed by Scott, Hanway and Edwards (1958) to the fact that H is a more effective replacing cation than Na.

The relative efficiency of the three extractants can be evaluated only when enough K has been added so that the effect of replaced $NH_4$ became relatively minor in each solution, that is, when the blocking effect in each case was made comparable. Under these circumstances the amount of $NH_4$ removed increased with decreasing initial pH of the extractant.

The amount of K required to produce the maximum blocking effect also varied with the solution pH. A K to Na ratio of 0.5 was necessary in the NaCl-HCl solution at pH 1, whereas a ratio in the vicinity of 0.2 served to reduce the amount of $NH_4$ removed to a minimal figure in the case of the other extractants. In the presence of maximum blocking the 1 N NaOH, 1 N NaCl and 1 N NaCl-HCl solutions removed essentially the same amount of $NH_4$ from vermiculite 2B as 1 N KOH, 1 N KCl, and 1 N KCl-HCl solutions respectively, at corresponding pH levels. That is, the Na was not replacing any $NH_4$ that was not exchangeable with K.

To investigate the pH-K blocking relationships in the acid

range in more detail vermiculite 2B samples were extracted with 1 N NaCl solutions that were adjusted to 4 pH levels by adding HOAc or HCl. These extracting solutions also contained 0 to 10 me. added K per 100 ml. As before, 1 g. samples of vermiculite 2B were refluxed in the extractants for 1 hour, filtered and the $NH_4$ in the filtrates were determined by distillation. The results obtained with 1 N NaCl pH(5.8), 1 N NaCl-0.1 N HOAc (pH 4 by adding NaOH), 1 N NaCl-0.1 N HOAc(pH 2.7) and 1 N NaCl-0.1 N HCl (pH 1) are shown in figures 2 and 3.

In figure 2 the data are plotted to show the effect of different levels of added K on the amount of $NH_4$ removed by each of the extractants. Again, as shown in figure 1, the amount of $NH_4$ removed decreased as the level of added K increased. In addition, however, it can be seen that the effect of the K at all levels of addition decreased progressively as the acidity of the solution increased. Apparently the blocking effect of K is related to the activity of the H ions in solution rather than to the potential acidity of the system. At least, 1 N NaCl-0.1 N HCl(pH 1) and 1 N NaCl-0.1 N HOAc(pH 2.7) removed different amounts of $NH_4$ at the same level of added K.

To give a clearer picture of the relationship between K blocking and the acidity of the extracting solution over the whole pH range, the percentages of the total $NH_4$ removed by the 1 N Na solutions have been plotted in figure 3 as a function of the initial pH of the extracting solution. It is apparent that the blocking effect of a given level of added K decreased with

Figure 2. Effect of added K on the extraction of $NH_4$ from $NH_4$-saturated vermiculite 2B by boiling 1 g. samples for 1 hour in 100 ml. of 1 N NaCl solutions adjusted to various initial pH levels with HCl and HOAc.

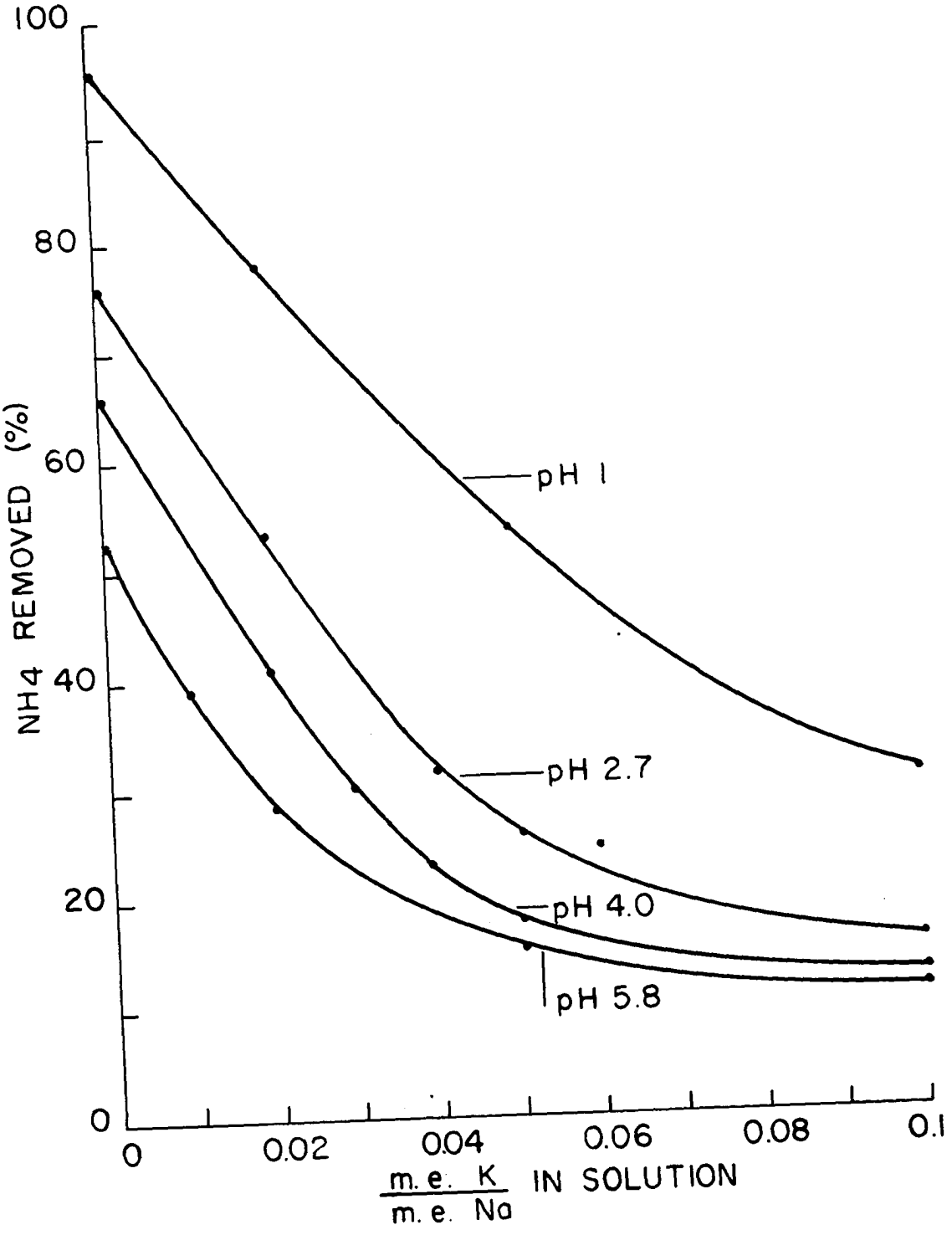
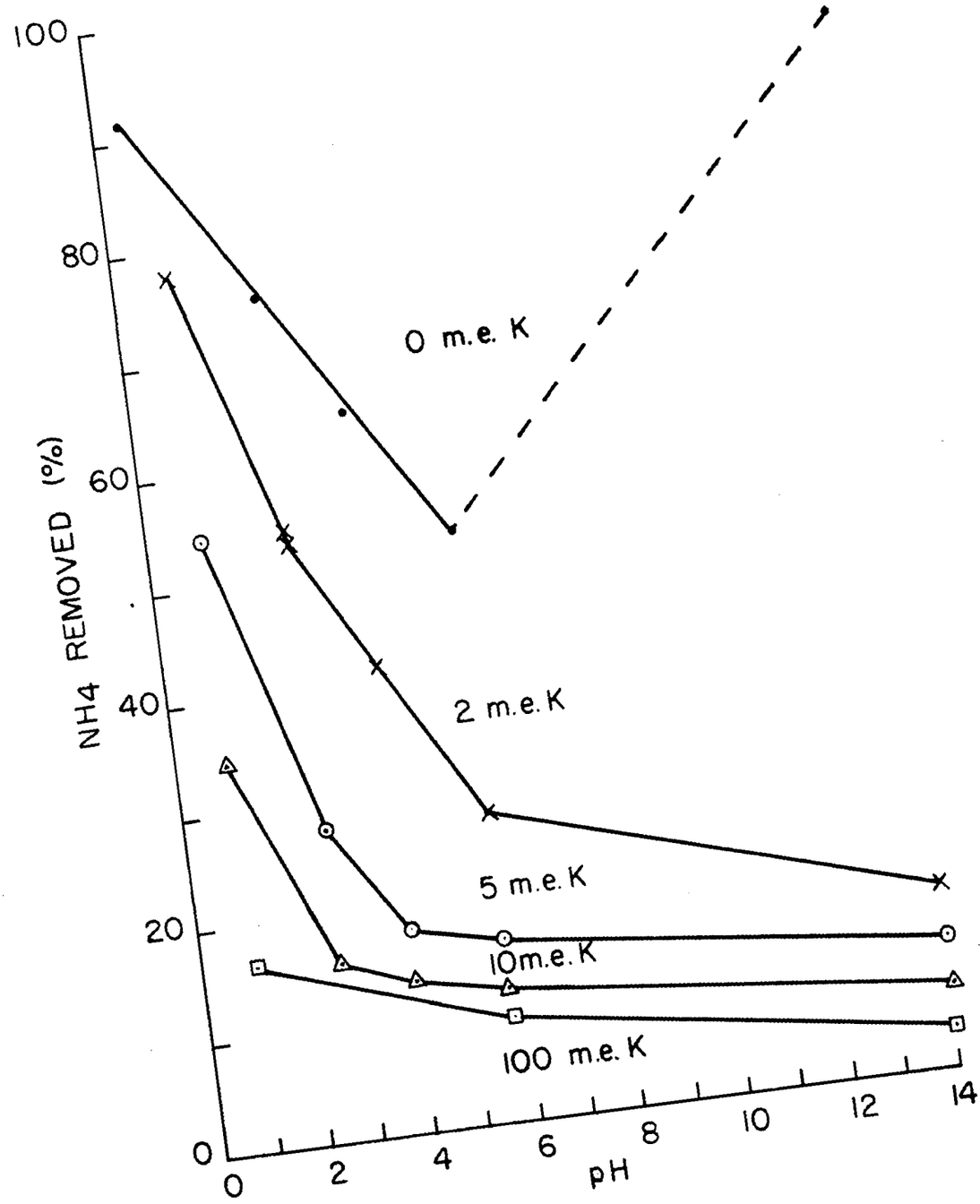

100
80
60
40
20
0
NH4 REMOVED (%)
pH 1
pH 2.7
pH 4.0
pH 5.8
0
0.02
0.04
0.06
0.08
0.1
m.e. K / m.e. Na IN SOLUTION

Figure 3. Effect of the pH of the extractant on the extraction of $NH_4$ from $NH_4$-saturated vermiculite 2B by boiling 1 g. samples in 100 ml. of 1 N Na solutions with various levels of added K.


100
80
60
40
20
0
NH4 REMOVED (%)
0 m.e. K
2 m.e. K
5 m.e. K
10m.e. K
100 m.e. K
0
2
4
6
8
10
12
14
pH

an increase in pH. Furthermore, the inverse relationship between blocking and pH persisted from pH 1 to 14. The relative effect of a given amount of blocking cation, however, varied with the degree of acidity. The rapid decrease in the amount of $NH_4$ removed when the pH of the extractant increased from pH 1 to 2.7 also occurred when Scott, Hanway and Edwards (1958) used 0.1 N acid solutions without added K. This would suggest that the H ion concentrations in this range were especially critical in relation to their effect on blocking by small amounts of both K and $NH_4$.

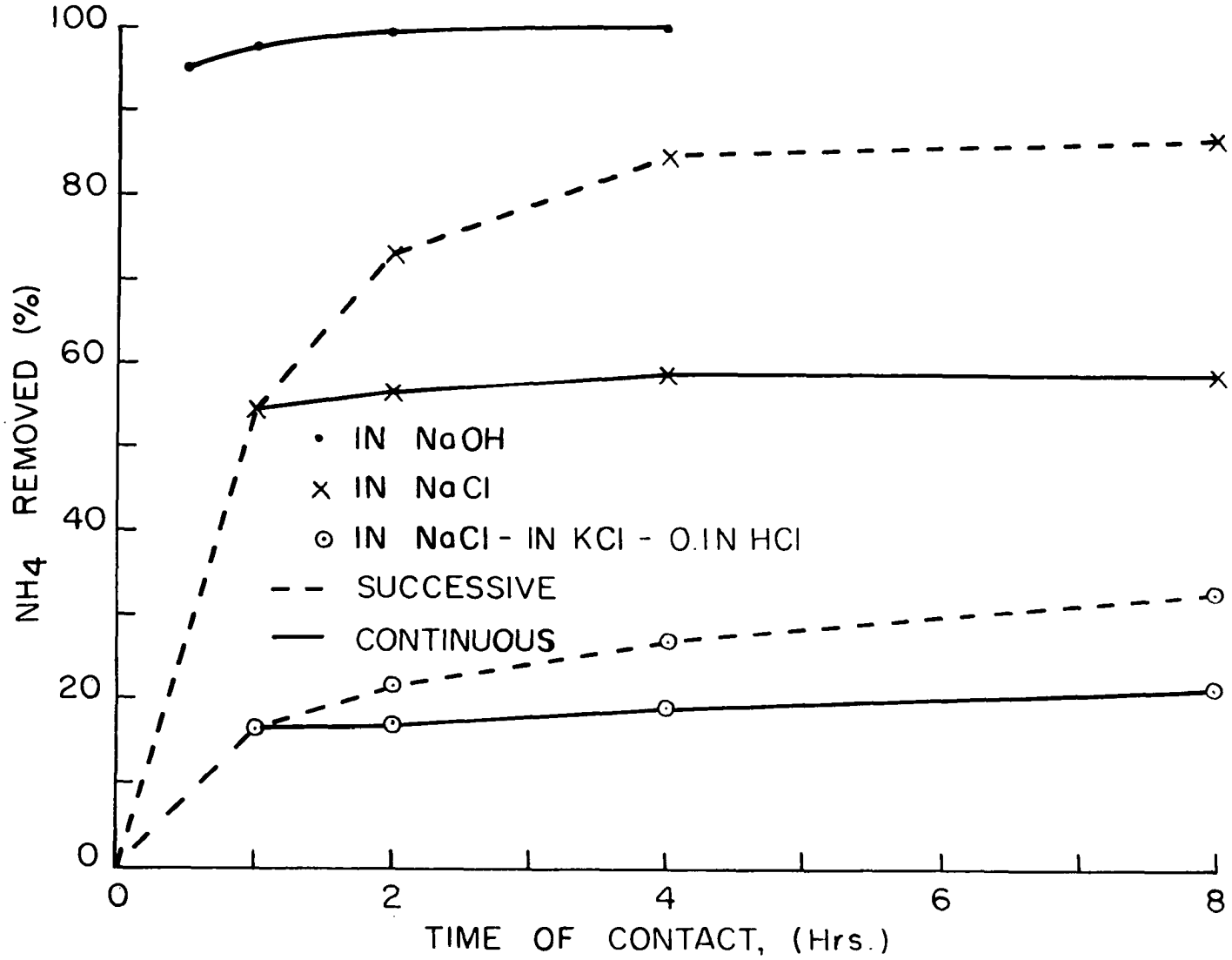
The results obtained when no K was added were particularly interesting because the effect of pH on the blocking effect of $NH_4$ and the removal of $NH_4$ by volatilization were both involved. When the solution pH was below 6 the extracted $NH_4$ accumulated in solution and a linear decrease in the amount of $NH_4$ removed occurred as the pH increased. On the other hand, when the solution pH was above neutral this relationship did not persist because the replaced $NH_4$ was not accumulating in solution. Therefore the alkaline solution was as effective, or even more effective, than the acid solution in removing $NH_4$ from vermiculite when no K had been added. Both effects of the extraction pH must be considered in any study of the displacement of ammonium.

In the discussion of the results plotted in figure 1 it was noted that the minimum amount of $NH_4$ removed by each 1 N Na solution containing added K approximately equalled that removed

by a 1 N K solution at the same pH. That is, the Na did not remove any $NH_4$ that was not displaced by K. Furthermore, Scott, Hanway and Edwards (1958) showed that the amount of $NH_4$ removed from vermiculite by 1 N KCl is not influenced by the accumulation of small amounts of displaced $NH_4$ in solution, since successive treatment of a clay sample with several increments of fresh 1 N KCl solution failed to remove more $NH_4$ than a single continuous extraction over the same total time period. Information as to the effect of the displaced ammonium on the extraction of $NH_4$ by neutral and acidic 1 N Na solutions in the presence of excess K was, however, still unavailable. Therefore it was decided to compare the results obtained in successive and continuous extractions of $NH_4$-vermiculite with both 1 N NaCl-1 N KCl-0.1 N HCl(pH 1) and 1 N NaCl(pH 5.8).

Samples of vermiculite 2B were boiled in NaCl and NaCl-HCl solutions in flasks fitted with reflux condensers, using 1 g. of clay to 100 ml. of solution. In the continuous extractions the same sample was equilibrated in the same volume of solution for a period of 1, 2, 4, and 8 hours. In the successive extractions, the samples were separated from the extracting solution and fresh solution was added at the end of 1, 2 and 4 hour periods of contact. Both the continuous and successive extraction values are plotted in figure 4 as percentage $NH_4$ removed from vermiculite 2B for times of contact of 1, 2, 4 and 8 hours. In the case of the successive extractions the cumulative amounts of $NH_4$ removed are plotted. The values obtained by

Figure 4. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by continuous and successive boiling extractions with 1 g. samples in 100 ml. extracting solution.


100
80
60
40
20
0
NH4 REMOVED (%)
0
2
4
6
8
TIME OF CONTACT, (Hrs.)
• IN NaOH
× IN NaCl
⊙ IN NaCl - IN KCl - 0.1N HCl
SUCCESSIVE
CONTINUOUS

continuous distillation of 1 g. of vermiculite 2B in 100 ml. of 1 N NaOH are also plotted in figure 4 to provide the comparison of the amount of $NH_4$ removed in a system free of blocking effects.

The continuous extraction in boiling 1 N NaCl did not remove any additional $NH_4$ after 4 hours of contact. Successive extractions raised the level of removal by over 20 percent, but the shape of the curve would indicate that complete removal of the $NH_4$ occupying interlayer positions would not be possible with this solution. From a comparison of the curves for NaCl and NaOH it would appear that, even in the absence of K, extremely small amounts of $NH_4$ in solution block the release of the ammonium remaining in the clay on relatively inaccessible exchange sites. The NaCl-KCl-HCl solution (pH 1), even though 1 N in K, removed more ammonium each time fresh solution was added. In the case of the continuous extractions, on the other hand, a condition approaching equilibrium appears to have been reached in less than 8 hours of contact. Thus, even in the presence of a large excess of K ions, the small amount of displaced $NH_4$ in this acid solution influenced the replacement of $NH_4$ occupying interlayer positions.

It is impossible to treat clays or micas with even dilute solutions of strong mineral acids to replace interlayer cations without some destruction of the clay lattice. However, the $NH_4$ that accumulated in solution during a continuous extraction of $NH_4$-saturated vermiculite with 0.1 N HCl was shown by Scott,

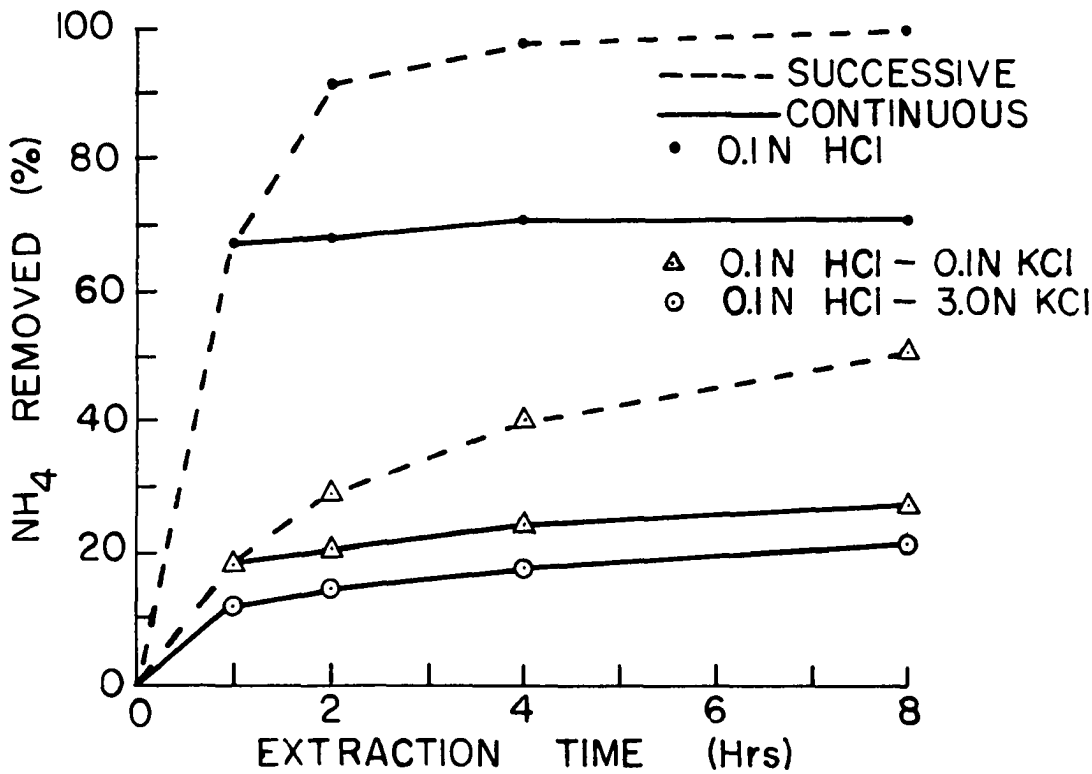
Hanway and Edwards (1958) to result in a maximum level of release of the fixed cation which was 30 percent below the level achieved with successive extractions using the same acid solution. Furthermore, it has been found that added K in neutral and alkaline extracting solutions affects the level of removal and not the rate of release by exchange or clay destruction. Consequently, additions of K were made to both 0.1 and 0.5 N HCl solutions to determine if this K would not only block the release of interlayer cations but also reduce the destruction of the lattice by strong acids.

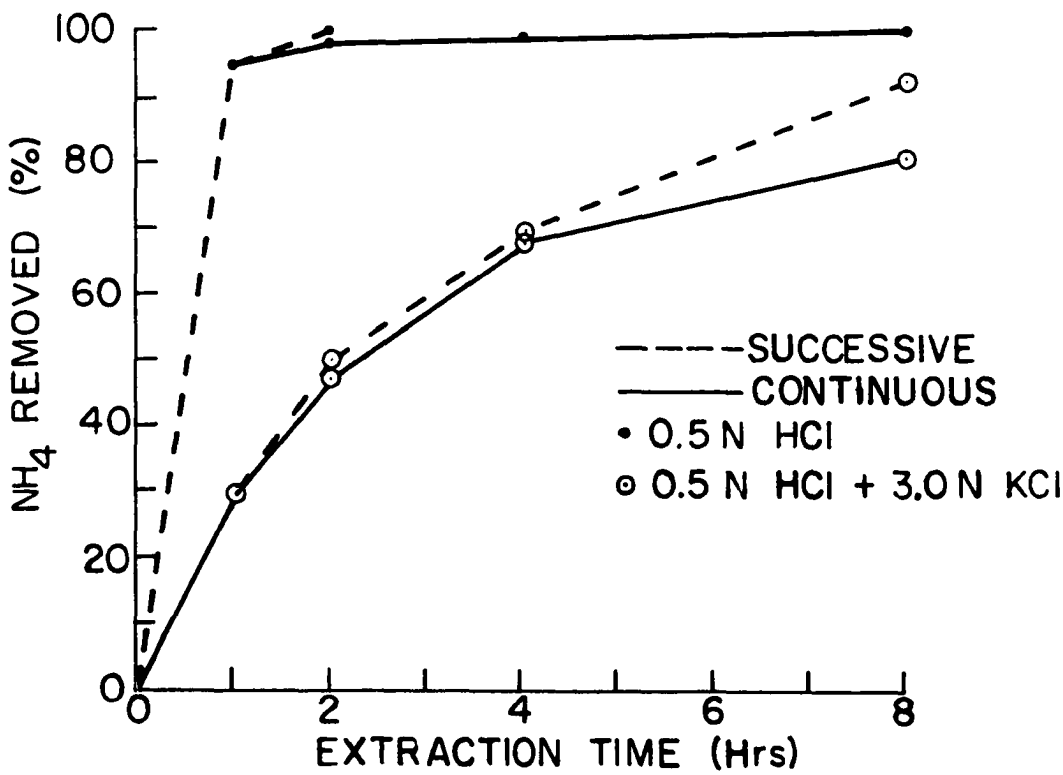
Samples of vermiculite 2B (1.0 g.) were placed in 250 ml. erlenmeyer flasks fitted with reflux condensers and were boiled in 100 ml. of 0.1 N HCl made 0.1 N and 3.0 N in KCl, continuously and successively for 1, 2, 4, and 8 hours. The percentage of the total $NH_4$ removed in each case is shown in figure 5. The results obtained with the same procedure but using 0.5 N HCl and 0.5 N HCl-3.0 N KCl are presented in figure 6.

Although the successive extractions with 0.1 N HCl, as shown in figure 5, finally removed all of the $NH_4$ from the vermiculite, the flattening of the curve for continuous extraction indicates that the $NH_4$ which accumulated in solution blocked the further release of $NH_4$ still present in the clay. The addition of enough KCl to make the acid solution 0.1 N in K merely slowed down the rate at which the $NH_4$ was removed in the successive extractions. Where 0.5 N HCl was used as the extractant (figure 6) neither the accumulation of $NH_4$ nor the

Figure 5. Effect of added K on the amount of $NH_4$ removed by continuous and successive boiling extractions with 1 g. vermiculite 2B in 100 ml. 0.1 N HCl solutions.

Figure 6. Effect of added K on the amount of $NH_4$ removed by continuous and successive boiling extractions with 1 g. vermiculite 2B in 100 ml. 0.5 N HCl solutions.


100
80
60
40
20
0
$NH_4$ REMOVED (%)
0
2
4
6
8
EXTRACTION TIME (Hrs)
SUCCESSIVE
CONTINUOUS
• 0.1 N HCl
△ 0.1 N HCl – 0.1N KCl
⊙ 0.1 N HCl – 3.0N KCl


100
80
60
40
20
0
$NH_4$ REMOVED (%)
0
2
4
6
8
EXTRACTION TIME (Hrs)
SUCCESSIVE
CONTINUOUS
• 0.5 N HCl
⊙ 0.5 N HCl + 3.0 N KCl

addition of K to a concentration of 3 N entirely blocked the release. That is, the presence of K in the acid solutions has affected the rate of replacement of interlayer $NH_4$ rather than the total amount replaced as in the neutral salt solutions. This would suggest that lattice destruction was occurring in the acid solutions. Visual evidence would support this hypothesis. It was observed that, in the mineral acids, large, bronze-colored vermiculite flakes were bleached around the edges and the decolorized area spread from the outside towards the middle with increasing time of contact. The bleached material dissolved readily in NaOH. When K was added the rate of attack on the vermiculite flakes was much reduced.

Boiling acid and salt solutions were used in the preceding experiments on the blocking effects of K and $NH_4$ in order to make these extractions comparable, with respect to temperature, to the alkaline distillations. Room-temperature leaching procedures are more often used, however, for the replacement of cations with salt or acid solutions. Scott, Hanway and Edwards (1958) found that acidified salt and acid solutions did not remove as much $NH_4$ from vermiculite when room temperature leaching techniques were employed instead of boiling extractions. Also, in the same paper the authors demonstrated that the acidification of 1 N NaCl and 1 N KCl solutions with 0.1 N HCl had less effect on the amount of $NH_4$ removed from vermiculite when the solutions were used for leaching as opposed to boiling extractions. A comparison of the effect of K added to neutral

and acidified NaCl leaching solutions with the effects already noted for the boiling extractions was therefore made.

Solutions of 1 N NaCl and 1 N NaCl-0.1 N HCl that were also 0.005, 0.01 and 0.02 N with respect to K were used as extractants. Separate 1 g. samples of vermiculite 2B were leached for a period of 1 hour with 400 ml. of each of the above solutions. The results are compared in table 4 with data obtained by refluxing 1 g. samples of this vermiculite in 100 ml. of the same solutions.

It is evident from the data in table 4 that added K interfered with the removal of the $NH_4$ in vermiculite by a leaching method just as it did in the boiling extraction techniques. The data also confirms the observation that the acidity of the extracting solution had a greater effect at the higher temperature. Part of this effect may have been due to a greater degree of acid destruction of the lattice. Furthermore, the blocking effect of added K, although apparently less in the leaching method, may have been confounded by differences in temperature and solution volumes used. The extraction methods also differed in regard to the accumulation of replaced $NH_4$. Therefore the magnitude of the blocking effects in the two methods cannot be directly compared. A more valid comparison of blocking effects in the two methods of extraction would result from the contrast between leaching and successive extraction using the same total volume of solution over the same total time interval in the two techniques.

Table 4. Percentage $NH_4$ removed from vermiculite 2B in 1 hour by leaching at room temperature compared to boiling equilibrations in the same solutions

| Extracting solution | $NH_4$ extracted (%) | |
|---|---|---|
| | Leached 1 hour | Refluxed 1 hour |
| 1 N NaCl | 73.4 | 52.7 |
| 1 N NaCl-0.005 N KCl | 63.7 | - |
| 1 N NaCl-0.001 N KCl | 62.2 | 39.7 |
| 1 N NaCl-0.02 N KCl | 58.8 | 24.0 |
| 1 N NaCl-0.1 N HCl | 81.1 | 95.6 |
| 1 N NaCl-0.1 N HCl-0.005 N KCl | 78.9 | - |
| 1 N NaCl-0.1 N HCl-0.01 N KCl | 78.2 | - |
| 1 N NaCl-0.1 N HCl-0.02 N KCl | 77.2 | 77.8 |

By way of a summary of the information obtained on blocking effects in the foregoing section, it can be said that added K or displaced $NH_4$ in Na solutions has less effect on the amount of $NH_4$ removed from vermiculite as the initial pH of the extracting solution is lowered. Under strongly acid conditions, attack upon the vermiculite lattice is apparently involved in $NH_4$ removal and blocking cations are able to slow down the rate of attack since the H ions must enter from the edges of the crystal. Under neutral conditions the presence of a certain amount of K relative to the displacing ion will permit only a definite amount of $NH_4$ to be displaced. This amount may be

increased by using a successive extraction method to reduce the amount of displaced $NH_4$ that is allowed to accumulate in solution, but the total amount of $NH_4$ removed remains below the complete displacement of the $NH_4$ in vermiculite possible with a K and $NH_4$-free extractant.

## Extractions with Cation Exchange Resins

The removal of $NH_4$ from a fixing mineral by means of a single equilibration in neutral or acid salt solutions has been shown to lack efficiency because of the accumulation of displaced $NH_4$ in the solution phase. Where K is also present in interlayer positions, as is the case with the vermiculite-biotite mixtures, there is always the possibility of additional interference with exchange of fixed $NH_4$ due to the release of K into solution. One method of reducing the amounts of displaced $NH_4$ and K capable of affecting the clay exchanger in a closed system would be to use an insoluble anion in the form of a cation exchange resin instead of a completely soluble salt. A comparison of salt and resin extractions was therefore made to determine whether or not there was less blocking, and therefore more $NH_4$ removed, where the cation exchange resin was employed.

The resin used throughout this study was Amberlite IR-120 obtained commercially in the Na form and saturated with various cations by leaching procedures using 1 N HCl, KCl, NaCl and $NH_4Cl$ solutions. After washing with large volumes of $NH_4$ and K-free distilled water until free of chlorides, the resins were

dried at 25°C and an atmospheric relative humidity of approximately 30 percent. The ease of handling in this condition made drying a desirable practice. They were then sieved under the same atmospheric conditions and the particles retained on a 32 mesh screen were collected for extraction purposes. The moisture contents of the >32 mesh Na-saturated materials prepared in this manner were approximately 20 percent. The cation exchange capacity of the air-dried, Na-saturated Amberlite was 517 me. per 100 g., oven dry basis.

For purposes of convenience, the resins will be designated simply as HR, $NH_4R$, KR, $NaR_o$ and $NaR_1$. The distinction between the two Na-saturated Amberlites was made due to the fact that different amounts of H were found on two successive batches prepared. Using both direct titration of the H on the resins in the presence of an excess of NaCl to the end point of bromthymol blue, and titration of the H removed by leaching with NaCl, the amounts of H on the $NaR_o$ and $NaR_1$ were found to be 0.5 and 27.5 me. per 100 g. air dry resin, respectively.

In order to extract the $NH_4$ from the vermiculite with a resin, the vermiculite and resin particles had to be mixed together in water. The presence of two cation exchangers with overlapping particle size ranges in such a system, however, leads to complications where an ion, ($NH_4$ in this case), present in both exchangers, must be removed from one but not from the other. The ideal answer to the problem, of course, would be a leaching solution that was completely selective with

respect to one exchanger as far as the cation of interest was concerned. The use of such a solution would circumvent the need for separating the clay from the resin before the cation on the resin was displaced and determined. Fortunately, K salts remove very little $NH_4$ from vermiculite even when the clay is $NH_4$-saturated, but are effective in removing $NH_4$ from a sulfonic acid type of cation exchanger. In order to establish whether or not leaching the replaced $NH_4$ from the resin-vermiculite mixture with KCl was a suitable practice, however, the results obtained by leaching the resin-vermiculite mixture, and the resin alone after separating it from the vermiculite, were compared.

Samples of Montana vermiculite 2B containing particles $<2$ mm. in diameter, were equilibrated with $>0.5$ mm. beads of HR and $NaR_1$ in 50 ml. erlenmeyers using 0.2 g. of vermiculite, 2 g. of air-dry resin and 20 ml. of $NH_4$-free distilled water. After constant agitation in a wrist-action shaker for 48 hours at 25°C, some of the samples were sieved, using suction, through 80 mesh stainless steel screens in plastic mounts that were held in Buchner funnels by rubber rings. The clay passing through the sieves was collected on filter papers in the funnels, and the clear filtrate, plus a small volume of wash water that was passed through both resin and clay, were collected for addition to the KCl or NaCl leachates from the resin. The remainder of the resin-vermiculite samples were filtered directly using Buchner funnels and suction. The separated resin and the

clay-resin mixtures were subsequently leached with 350 ml. of 1 N KCl or 1 N NaCl added in small portions and with the use of suction only to remove the last residues of each addition before applying more solution. The $NH_4$ was determined by adding KOH to the KCl or NaCl leachate and distilling into saturated boric acid, followed by titration with standard 0.01 N HCl using methyl red-methylene blue as an indicator. The results in terms of me. of $NH_4$ per 100 g. of oven-dry clay recovered in the leachate, are given in table 5. The clay contained a total of 82.1 me. of $NH_4$ per 100 g.

Table 5. $NH_4$ extracted from $NH_4$-saturated Montana vermiculite 2B by equilibrating 0.2 g. of clay with 2 g. of HR and NaR for 48 hours and subsequently leaching the resin (sieved) or the clay and resin together (unsieved) with 350 ml. of 1 N KCl or NaCl

| Leaching solution | Pre-leaching procedure | $NH_4$ extracted, me./100 g. | |
|---|---|---|---|
| | | HR | $NaR_1$ |
| KCl | sieved | 80.5 | 69.9 |
| | unsieved | 80.8 | 71.0 |
| NaCl | sieved[a] | 79.5 | - |
| | unsieved | 81.0 | - |

[a]20 ml. $H_2O$ present during equilibration discarded.

Slightly higher values were obtained where clay and resin were leached together. These differences may be due to the removal of $NH_4$ from the clay by the leaching solutions. However, even though the air-dry resin samples were sieved to $>0.5$ mm.

bead size before use, there appeared to have been some breakdown of the resin particles during the equilibration period. Consequently, some $NH_4$ may have been lost along with resin fragments passing through the sieve. Since the differences between the sieved and unsieved results were small when KCl was used, and since the relatively coarse vermiculite did not interfere with the KCl leaching, the resin and vermiculite were leached together in subsequent experiments. The use of 1 N KCl was also made standard practice because it was possible that NaCl could remove $NH_4$ from the vermiculite if the level of removal of $NH_4$ from the clay by the resin prior to leaching was not as nearly complete as it was with the HR in this experiment. Based on observations made in this experiment, another procedure adopted was the addition of an amount of 1 N KCl at least equal to the volume of water present in the clay-resin mixture about 10 minutes prior to filtering in order to flocculate the highly dispersed clay that was invariably present, even with originally coarse vermiculite, following a resin treatment.

In order to compare the amounts of $NH_4$ that salts and resins would extract from vermiculite at room temperature, it was first necessary to determine the extraction period required for each extractant. Therefore, the effect of time of contact of the vermiculite with the salt or resin upon the amount of $NH_4$ removed was determined.

In these time studies, separate 0.2 g. samples of vermiculite 2B were shaken continuously at 25°C with 20 ml. of 1 N

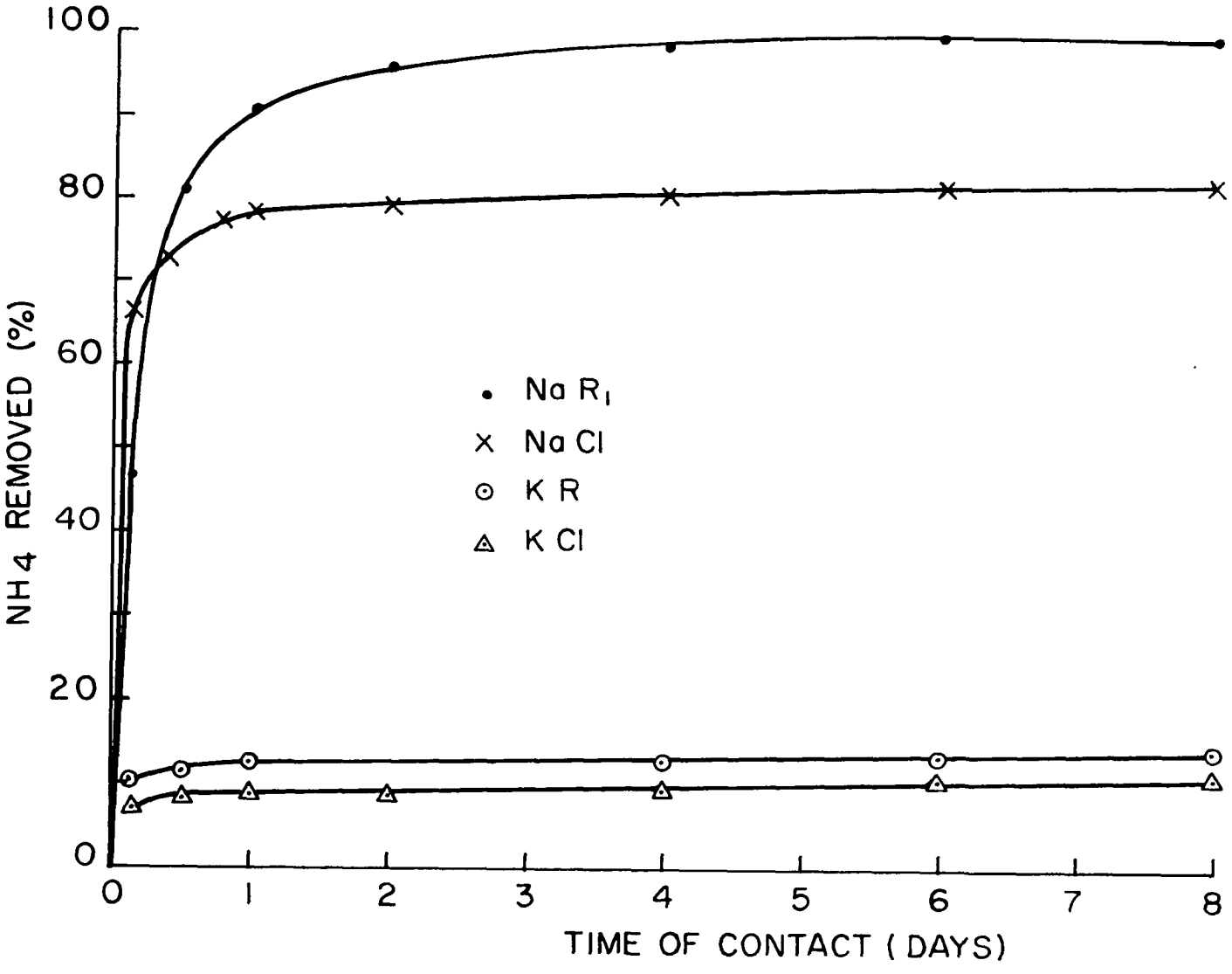
KCl, 1 N NaCl or with sufficient resin to give 20 me. of K or Na in 20 ml. of $H_2O$. Times of contact ranged from 3 hours to 8 days. The results, expressed as the percentage removal of $NH_4$ from the vermiculite, based on the total content of 82.1 me. of $NH_4$ per 100 g. of clay on an oven-dry weight basis, are presented graphically in figure 7.

The time required to reach maximum removal by the NaCl and $NaR_1$, appears to be somewhere between 4 and 8 days. The amount of $NH_4$ released subsequent to the first 24 hours of contact was small for all of the extractants, amounting to 1 to 2 percent for the KR, KCl and NaCl and about 7 percent to the $NaR_1$. Based on the results of this experiment a shaking time of 8 days was used in subsequent resin and salt extractions at 25°C.

The initial rate of removal of the $NH_4$ in the vermiculite was less by $NaR_1$ than by NaCl. Since the $NH_4$ involved at this stage was either exchangeable or fixed near the crystal edges, the supply of displacing cations in solution was a factor in determining the rate of displacement. However, after the initial phase the rate at which the $NH_4$ was removed was slow with both the resin and salt and both required from 4 to 8 days to remove their maxima. This last phase apparently involved the slow release of $NH_4$ from interlayer positions.

Using the 8 day period of equilibration, a comparison was made of the effectiveness of salt and resin extractions in removing the $NH_4$ in the undegraded vermiculite-biotite sample 2B and in the degraded vermiculite 3D. Samples of vermiculites

Figure 7. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by equilibrating 0.2 g. of clay with 20 me. of Na as NaCl and $NaR_1$ and with 20 me. K as KCl and KR, in 20 ml. $H_2O$, as affected by time of contact.


100
80
60
40
20
0
NH4 REMOVED (%)
Na R1
Na Cl
K R
K Cl
0
1
2
3
4
5
6
7
8
TIME OF CONTACT ( DAYS)

2B (0.2 g.) and 3D (0.1 g.) were extracted with 20 me. Na as NaCl and $NaR_1$ and with 20 me. K as KCl and KR, each in 20 ml. of solution. The equilibrations were carried out at 25°C with continuous agitation. The results obtained in this experiment, expressed in me. $NH_4$ per 100 g. clay on an oven dry (110°C) basis, are presented in table 6. The total $NH_4$ (by Kjeldahl) and the amount extracted by distilling 1 g. clay in 100 ml. 1 N KOH for 2 hours are also included for comparison. The $NH_4$ removed by KOH distillation was arbitrarily considered to be exchangeable $NH_4$.

Table 6. Comparison of the $NH_4$ removed from $NH_4$-saturated vermiculites 2B and 3D by K and Na saturated resins and their corresponding chloride salts

| Treatment | Extraction time | $NH_4$ removed, me./100 g. | |
|---|---|---|---|
| | | Vermic. 2B | Vermic. 3D |
| Kjeldahl digestion | 12 hours | 82.1 | 157.7 |
| KOH distillation | 2 " | 2.8 | 5.2 |
| $NaR_1$ | 8 days | 81.1 | 154.1 |
| NaCl | " | 66.8 | 77.6 |
| KR | " | 11.5 | - |
| KCl | " | 8.9 | 7.1 |

Much of the $NH_4$ in both the degraded and undegraded vermiculites was not replaceable by K, since the KOH distillation values are very low. KCl, at a lower pH, is somewhat more

effective than the hydroxide. However, the use of KR instead of KCl did not increase the recovery of $NH_4$ from the vermiculites to any extent. The slight increase in recovery by the resin as compared to the salt could be due to the grinding and dispersing effect of the resin particles on the clay over an 8 day shaking period.

The most striking feature of the results in table 6 is the fact that $NaR_1$ removed most of the $NH_4$ in both degraded and undegraded vermiculites. If the distribution coefficient for the exchange of cations between the two exchangers was equal to 1, 81.3 and 156.4 me. of $NH_4$ should have been removed from vermiculites 2B and 3D, respectively, by the 20 me. of Na on the resin. The actual recoveries of 81.1 and 154.1 me. with $NaR_1$ are therefore close to the theoretical values. On the basis of cation concentrations the NaCl should have removed as much $NH_4$ as the resin. The fact that NaCl does not remove $NH_4$ from vermiculite effectively has already been shown to be due to the blocking effect of the displaced $NH_4$ which accumulates in solution. The point to be solved then, is why NaR was more effective than NaCl in extracting fixed $NH_4$ from the vermiculites.

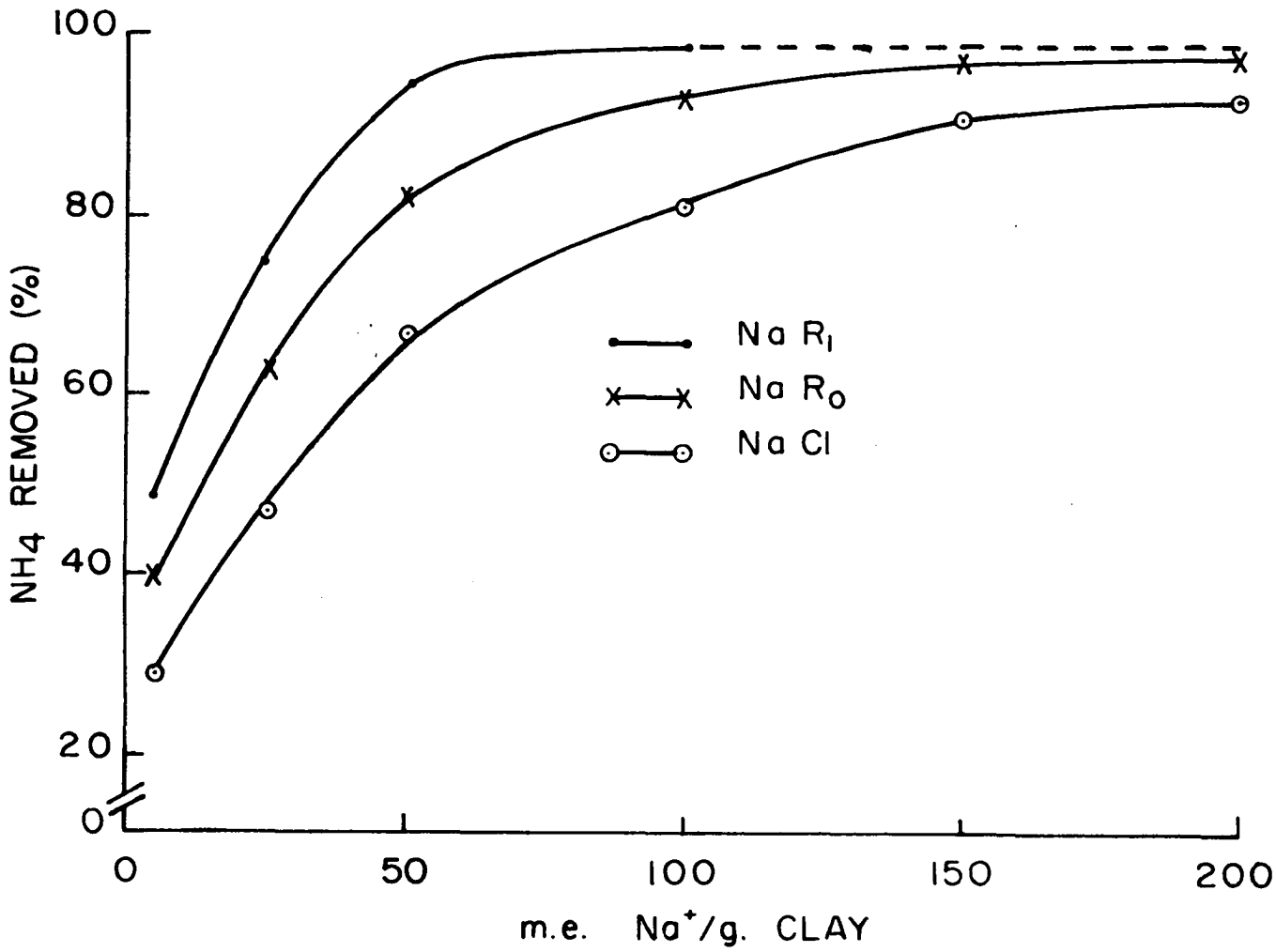
In order to establish the causes underlying the effectiveness of $NaR_1$, experiments were initiated to investigate a number of factors known to affect $NH_4$ removal by salt solutions, such as concentration of the displacing cation, acidity, and accumulations of fixable cations in solution. A comparison of the amounts of $NH_4$ removed from vermiculite by NaCl, $NaR_1$, and $NaR_o$

at different Na ion concentrations is presented in figure 8. These data were obtained by treating 0.2 g. samples of vermiculite 2B at 25°C for 8 days with different amounts of the 2 resins in 20 ml. of $NH_4$-free water and various amounts of Na as NaCl in 20 ml. of solution. The values for the percentage $NH_4$ removed that are shown in figure 8 were calculated on the basis of a total of 82.1 me. $NH_4$ present per 100 g. of oven-dry clay.

Both of the resins and the NaCl extracted more $NH_4$ as the amount of Na was increased. This effect had been demonstrated previously for boiling NaCl extractions by Hanway, Scott and Stanford (1957). Resins, therefore, do not behave differently in this respect than comparable salt solutions. The $NaR_1$ and $NaR_0$ did, however, remove more $NH_4$ from vermiculite at all concentrations than the NaCl. However, the amount of Na in the resin required to remove a given proportion of the $NH_4$ was different for $NaR_1$, than for $NaR_0$. The $NaR_0$ did not displace, at any concentration of Na, as much $NH_4$ as the $NaR_1$ removed from the vermiculite at the 20 me. level.

As stated at the beginning of the present section, the reason for making a distinction between the two batches of Na-saturated Amberlite IR-120 was the fact that they were shown to carry different amounts of exchangeable H (27.5 me. on $NaR_1$ as opposed to 0.5 me. per 100 g. on $NaR_0$). In order to investigate the relationship between acidity and the amount of $NH_4$ removed during the resin extractions, a time study was conducted with HR, $NaR_1$ and $NaR_0$ at cation concentrations low enough to make

Figure 8. $NH_4$ removed from 0.2 g. samples of $NH_4$-saturated vermiculite 2B in an 8 day equilibration with varying amounts of Na as $NaR_1$ and $NaR_o$ in 20 ml. of $H_2O$, and as NaCl in 20 ml. of solution.

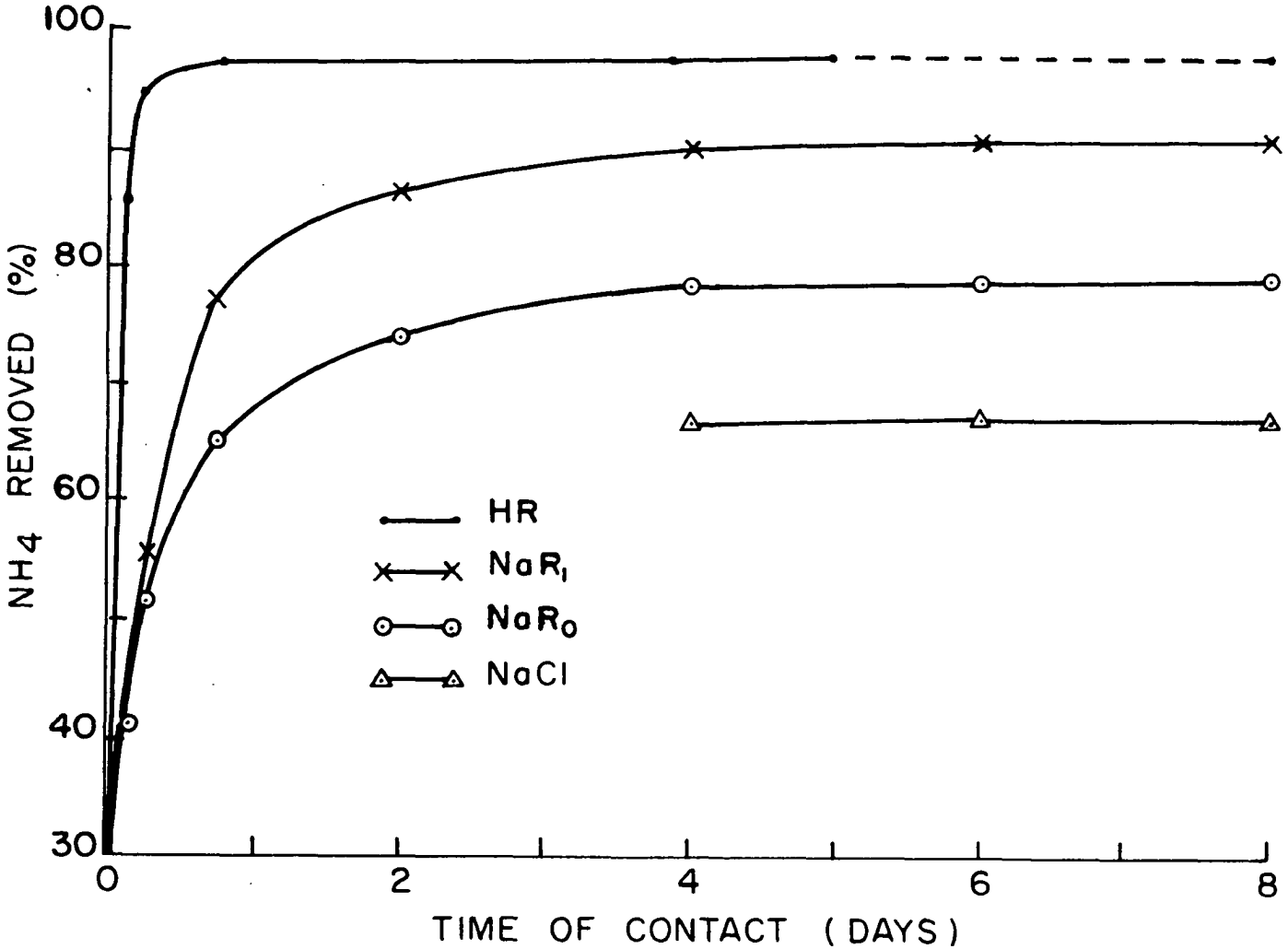

100
80
60
40
20
0
NH4 REMOVED (%)
0
50
100
150
200
m.e. Na+/g. CLAY
Na R1
Na R0
Na Cl

complete recovery of $NH_4$ improbable for any treatment. In this experiment 0.2 g. samples of vermiculite 2B were treated with 2 g. of HR, $NaR_1$, $NaR_o$ and with 10 me. of NaCl in 20 ml. of $NH_4$-free distilled water. The 2 g. portions of air dry HR, NaR and $NaR_o$ resin used contained 3.59 me. H, 0.56 me. H + 7.5 me. Na, and 0.01 me. H + 8 me. Na, respectively. The samples were shaken for periods ranging from 3 hours to 8 days at 25°C. The amounts of $NH_4$ removed, expressed as percentages of the $NH_4$ in the vermiculite, are shown in figure 9.

The rates of removal of $NH_4$ from vermiculite by the resins were in the order $HR > NaR_1 > NaR_o$. The HR removed its maximum within 24 hours, whereas the $NaR_1$ required 4 days and the $NaR_o$ even longer to reach equilibrium. Likewise, the total amount of $NH_4$ that was removed by each extractant was different and in the order $HR > NaR_1 > NaR_o > NaCl$. Thus, as far as the resins are concerned, the results are in line with the suggestion that differences are due to the amount of H present.

If the superiority of $NaR_1$ over $NaR_o$ as an extractant of $NH_4$ from vermiculite was due to the larger amount of H on the $NaR_1$, the difference should disappear if the level of H on the two resins is equalized. Samples of $NaR_1$ were therefore titrated with enough standard NaOH to reduce the amount of H on this resin to the same level as the H on the $NaR_o$. Also, to determine to what degree the difference between recoveries of $NH_4$ from vermiculite by NaCl and $NaR_1$ was due to the H on the resin, enough HCl was added to a 1 N NaCl solution to give the same

Figure 9. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by shaking 0.2 g. clay with 2 g. of HR, $NaR_1$ and $NaR_0$ in 20 ml. of $H_2O$, as affected by time of contact.


100
80
60
40
30
NH4 REMOVED (%)
0
2
4
6
8
TIME OF CONTACT (DAYS)
HR
NaR1
NaR0
NaCl

amount of H ions in 20 ml. of the salt solution as was present on 2 g. of $NaR_1$. Samples of vermiculite 2B (0.2 g.) were shaken for 8 days at 25°C with 10 me. of Na as $NaR_1$, $NaR_o$, NaCl, and the HCl-treated NaCl and the NaOH-treated $NaR_1$ described above. In each case the vermiculite and the extracting salt were mixed in 20 ml. of $NH_4$-free distilled water. The amounts of $NH_4$ removed by the various extractants, both in terms of me. $NH_4$ per 100 g. of clay on an oven-dry (110°C) basis and as percentage removal, are given in table 7.

Table 7. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by 10 me. Na as $NaR_1$, $NaR_o$ and NaCl as affected by adjusting the levels of H present

| Extractant | $NH_4$ removed | |
|---|---|---|
| | me./100 g. | percent |
| $NaR_o$ | 67.3 | 82.0 |
| $NaR_1$ + NaOH | 67.8 | 82.6 |
| $NaR_1$ | 78.2 | 95.3 |
| NaCl + HCl | 73.1 | 89.0 |
| NaCl | 55.0 | 67.0 |

The $NaR_1$ and $NaR_o$ produced essentially the same results when their H ion levels were made equal. Therefore it may be concluded that the difference between them was entirely due to the differences in levels of H on the exchange. As expected in view of previous work by Scott, Hanway and Edwards (1958), the

addition of HCl to NaCl markedly increased the amount of $NH_4$ removed from the vermiculite by the salt. However, even though the same amount of H was present in the NaCl + HCl and the $NaR_1$ systems, the salt solution was not as effective as the resin. This occurred in spite of the fact that the dissociation of H in the resin system was much less, and the pH therefore much higher, than in the NaCl-HCl mixture.

There are certain attributes of exchange resins which, if pertinent to the present study, might explain some or all of the difference between $NH_4$ removal by Na-saturated Amberlite IR-120 and NaCl. Since cation exchangers do not exhibit equal affinity for all ions (even if the valence is the same), and the affinity series for the same resin frequently changes with concentration, there is always the possibility of selective adsorption of one or more ions in a system. Therefore, the distribution coefficient ($K_D$) for the following exchange reaction in water was determined.

$$NaR_o + NH_4^+ + Cl^- \rightleftharpoons NH_4R_o + Na^+ + Cl^-$$

Starting with 9.64 me. of Na on the resin, and 10.06 me. $NH_4$ as $NH_4Cl$ in 20 ml. of $H_2O$, the resin and salt were shaken for 48 hours at 25°C. After equilibration the amounts of $NH_4$ on the resin and in solution were 4.67 me. and 5.39 me. respectively. The distribution coefficient was calculated by the following relationship and found to be 0.814.

$$K_D = \frac{[NH_4]_{R_o}\ [Na]_{soln}}{[Na]_{R_o}\ [NH_4]_{soln}} = \frac{[4.67]\ [4.67]}{[4.97]\ [5.39]} = 0.814$$

Under the conditions of this experiment, therefore the $NH_4$ was not taken up in proportion to its concentration in solution. Instead, the Na ions, on the resin to begin with, appeared to be preferred slightly in that phase. This particular Na-saturated resin should therefore show a lack of preference for $NH_4$ ions in solution. The explanation for the efficiency with which $NaR_o$ removes $NH_4$ from vermiculite cannot therefore lie in this direction.

When two cation exchange materials are mixed in water it is possible that the oscillation volumes of the adsorbed cations could overlap. Thus a type of contact exchange such as that postulated by Jenny and Overstreet (1939) might be possible and could increase the effective transfer of cations. To determine whether contact exchange was a factor contributing to the efficiency of the resins, experiments were conducted in which the resin and the $NH_4$-saturated vermiculite were separated by a visking membrane in machined plastic dialysis cells. These cells, designed for the purpose of this experiment, were built in such a manner that the resin could be removed by itself with no actual contact with the clay at any time. A sample of vermiculite 2B (0.2 g.) was weighed into the bottom well of each dialysis unit and 10 ml. of water or NaCl solution added to the clay. The visking membrane, previously soaked and kept moist, was then placed over the bottom cell, and the top unit screwed

down tightly to form a second compartment. The resin and 10 ml. of $H_2O$, or 10 ml. of a NaCl solution were added to the top compartment through a hole in the top face. This tapered hole was made sufficiently large so that the resin could be readily removed from the top cell by a stream of water from a wash bottle. The hole also served as a sump which could be varied in size, through the selection of stoppers, in order to keep the level of solution the same on both side of the membrane. The extractants used were $NaR_1$, NaCl and $NaR_1$ + NaCl to give in each case a total of 20 me. of Na.

The NaCl treatments were included to determine if the amount of $NH_4$ removed from the vermiculite would be affected by having the clay confined to 1/2 of the total volume of solution and therefore separated from part of the displaced $NH_4$. The mixtures of resin and NaCl, on the other hand, were included in case the exchange of cations was slow between the resin and clay when separated by a membrane. It was thought that a proper test of the role of contact exchange in resin extractions of vermiculite might not be possible over a practical extraction period unless the concentration of displacing cations in solution was increased.

Equilibrations were for 8 days at 25°C with gentle shaking of the circular cells placed on edge in a horizontal shaker. The results of the experiments are presented in table 8.

The separation of the resin from the clay by a membrane resulted in a slight (1.1 me.) reduction in $NH_4$ removed in 8

Table 8. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by $NaR_1$, $NaR_1$ + NaCl and NaCl as affected by separation of the clay from the resin or a portion of the extracting solution

| System | $NH_4$ removed (me./100 g.) |
|---|---|
| Clay + 20 ml. $H_2O$ + 20 me. Na as $N_aR_1$ | 81.1 |
| Clay + 10 ml. $H_2O$, membrane, 10 ml. $H_2O$ + 20 me. Na as $NaR_1$ | 80.0 |
| Clay + 20 ml. $H_2O$ + 10 me. NaCl + 10 me. Na as $NaR_1$ | 79.9 |
| Clay + 10 ml. $H_2O$ + 5 me. Na as NaCl, membrane, 5 me. Na as NaCl + 10 ml. $H_2O$ + 10 me. Na as $NaR_1$ | 79.7 |
| Clay + 20 ml. $H_2O$ + 20 me. Na as NaCl | 67.1 |
| Clay + 10 ml. $H_2O$ + 10 me. Na as NaCl, membrane, 10 me. Na as NaCl | 67.0 |

days. However, this difference is of about the same order of magnitude as that obtained in the experiment on the effect of sieving before leaching vs leaching resin and clay together (table 4). Since no sieving was used in the current experiment, the difference between the $NH_4$ recoveries by the resin of 81.1 me. (mixed) and 80.0 (separated) could be due entirely to this leaching technique that was used in removing displaced $NH_4$. Therefore, the efficiency of resins as extractants of $NH_4$ does not stem from contact exchange between resin and exchanger.

The presence of the membrane to separate 1/2 of the NaCl solution from the clay made no difference to the total $NH_4$

removed. This would confirm that the ratio of the fixable to displacing cations in the neutral solution dictates the amount of $NH_4$ removed rather than the actual quantity of fixable cations in contact with a given amount of clay.

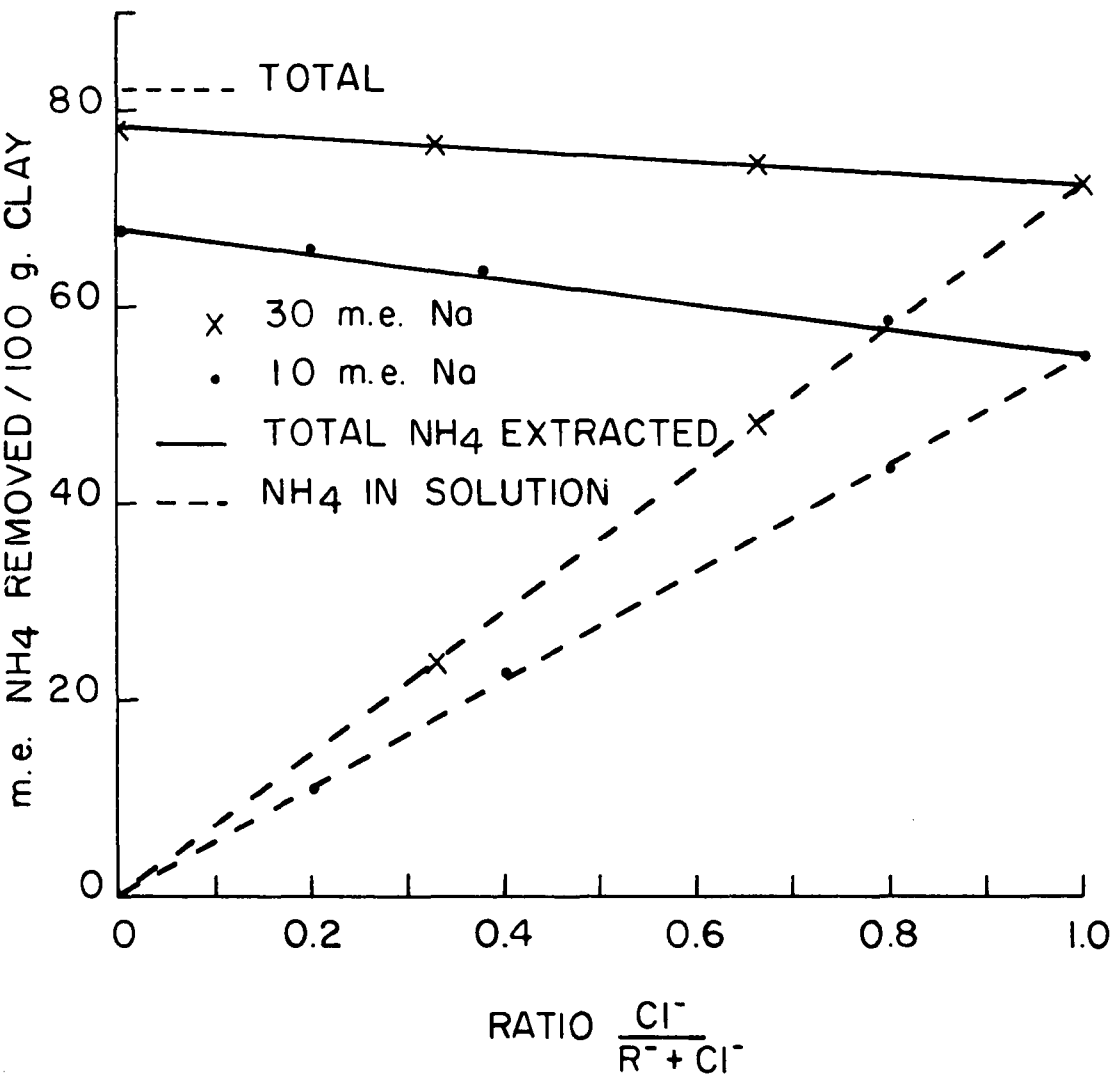
The addition of NaCl to the clay-resin system was apparently unnecessary, since exchange between resin and clay reached about the same level at 8 days of contact whether the membrane was present or not. It is possible that the rate of exchange was somewhat slower through the membrane since, as shown in figure 7, $NaR_1$ appeared to have extracted the maximum amount of $NH_4$ from vermiculite 2B in about 4 days. The 8 day contact time used in the present experiment could have allowed the clay-membrane-resin system sufficient time to overcome a slower rate. Apparently the presence of NaCl in the clay-resin mixture has reduced the total recovery of $NH_4$ from the vermiculite. Since the presence of 10 me. of Na as NaCl out of the 20 me. of Na present means that approximately 1/2 of the $NH_4$ displaced from the clay will remain in solution, the lowered recovery from the mixture could be explained on the basis of blocking effects.

It was decided to investigate further the relationship between the amounts of soluble anions in a clay-resin system, the total $NH_4$ removed from the clay and the proportion of this $NH_4$ that was in the solution phase. Samples of vermiculite 2B (0.2 g.) were treated with NaCl and $NaR_o$ alone and in mixtures to give the same total concentration of Na. Two experiments were carried out, one with only 10 me. Na to ensure that only

partial recoveries of $NH_4$ would be obtained even with the resin, and a second with 30 me. Na. The amounts of $NH_4$ on the resin and in solution were measured after 8 days of equilibration in the case of the 10 me. level of Na, and after 48 hours where the 30 me. of Na were used. The total $NH_4$ and the amount in solution for each determination are plotted in figure 10, against the ratio of soluble to total anions (or cations) present.

There was a linear relationship between the $NH_4$ in solution and the ratio of Cl to R + Cl, as could be expected. The total amount of $NH_4$ removed likewise showed a linear decrease, within the limits of the analytical errors, with increasing amounts of soluble anions. Therefore it is evident that the accumulation of $NH_4$ in solution determined the amount of $NH_4$ replaced when NaCl + NaR were present. The amount of $NH_4$ in solution when $NaR_o$ was used without NaCl was very small and could not be measured with the techniques used because of the small amounts of $NH_4$-vermiculite being extracted. Whether or not the small quantity of $NH_4$ in solution in the resin-clay systems due to hydrolysis was responsible for keeping resins from extracting all of the $NH_4$ from vermiculite is still not known. However, since it has been shown in the work with salts and bases that the presence of very small amounts of $NH_4$ in solution will prevent complete removal of the $NH_4$ from the clay even by successive extractions, this seems to be a reasonable explanation.

Figure 10. $NH_4$ removed from $NH_4$-saturated vermiculite by equilibrating 0.2 g. of clay with 10 and 30 me. Na in 20 ml. $H_2O$ as affected by the proportion of $NaR_o$ and NaCl present.


TOTAL
80
60
40
20
0
m.e. NH4 REMOVED / 100 g. CLAY
x 30 m.e. Na
• 10 m.e. Na
TOTAL NH4 EXTRACTED
NH4 IN SOLUTION
0
0.2
0.4
0.6
0.8
1.0
RATIO Cl⁻ / R⁻ + Cl⁻

To summarize briefly the results of the resin work with vermiculite, it can be said first that the main reason for the greater efficiency of the Na-saturated resins as compared to NaCl in removing $NH_4$ from the clay appears to be the lower concentration of fixable cations in solution to block further removal of interlayer ammonium. The somewhat higher results with KR as opposed to KCl could be due simply to the grinding effect of resin on the clay resulting in a somewhat greater release of $NH_4$. The HR was considerably more effective than the Na-saturated resins. Arnold (1958) also found that H-saturated Amberlite IR-120 was much more efficient than either the Ca- or Na-saturated forms of the resin in removing K from fixing minerals. The presence of small amounts of H on a predominately Na-saturated resin increased the effectiveness of the resin in removing the $NH_4$ in vermiculite, and the superiority of $NaR_o$ over NaCl was shown to be partly due to the H on the resin. It was demonstrated that the difference between NaCl and the Na-saturated resins were not due to selective adsorption of $NH_4$ by the resin or to contact effects. It was concluded that the difference between resin and salt not due to H was the result of the reduced blocking from $NH_4$ in solution.

## Particle Size

As pointed out by Wiklander (1955) a rapid exchange of ions is possible only where the exchangeable ions are directly accessible to the ions in solution, and slower rates will

result where the interchange must be preceded by diffusion into the inner surfaces of the exchanger. Kunin (1958), in discussing cation exchange kinetics, states that diffusion rates, rather than the actual speed of the transfer at the exchange sites, are generally accepted as being responsible for the overall rates of ion exchange. Working with relatively coarse phyllosilicates and concentrated extracting solutions, the length of the diffusion path within the particle is likely to be rate-determining from the beginning. The maximum length of this path for a circular clay plate is equal to the radius. Since, as observed by Barshad (1948) for vermiculite, the exchange progresses from the outside edges towards the middle, for particles of a given size the rate of exchange should decrease with time as the diffusion path lengthens. Likewise, the smaller the particle size the faster the rate of removal per gram of material.

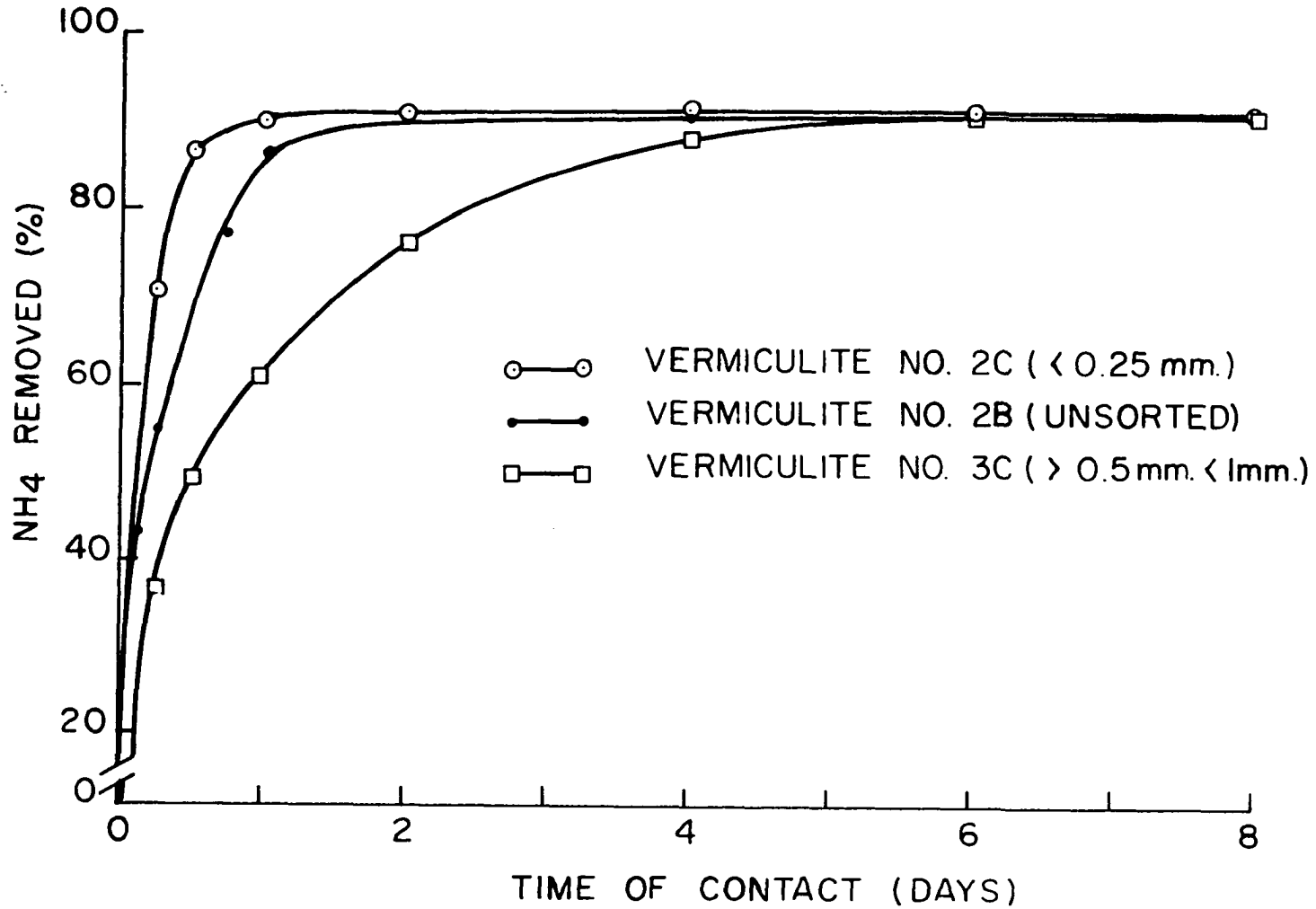
It has been demonstrated that the displacement of the naturally occurring interlayer K in the micas is made easier by grinding. Mackenzie and Milne (1953) found that grinding increased the cation exchange capacities of both vermiculite and biotite. However, no literature relative to the effect of particle size upon the rate of release of fixed $NH_4$ or K could be found, although Barshad (1948) reported a greater total amount of K was removed from finer biotite fractions after 3 weeks of leaching. The possibility also exists that particle size may influence the degree of blocking by a given ratio of

fixable to extracting cation. Barshad (1954b) considered ion "trapping" to be a phenomenon associated largely with unground vermiculite because he observed an increase in the amount of $NH_4$ removed from vermiculite by KOH as particle size decreased. A limited investigation was therefore made into the effect of particle size on the replaceability of $NH_4$ in vermiculite with several extraction techniques and different levels of added potassium.

Three $NH_4$-saturated vermiculites (2B, 2C and 3C) were equilibrated with $NaR_1$, using a ratio of 0.2 g. of clay to 2 g. of air dry resin. Sample 2B, an unsorted but $< 2$ mm. vermiculite, had been passed through a Christy and Norris laboratory hammer mill. The particle size distribution for this sample was the same as that given for sample 2A on page 34, thus approximately 50 percent by weight was material between 0.25 and 0.5 mm. in diameter. Sample 2C was obtained by grinding a portion of $NH_4$-saturated vermiculite 2B to pass a 60 mesh screen, that is, it was all $<0.25$ mm. in diameter. Sample 3C was coarse material ($>0.5$ mm. $<1.0$ mm. in diameter) sieved from $NH_4$-saturated vermiculite 3B. The resin and clay were shaken with 20 ml. of distilled water on a wrist action shaker for periods varying from 3 hours to 8 days. The results are presented in figure 11 expressed in terms of percentage $NH_4$ removed. Total $NH_4$ values for vermiculite samples 2B, 2C and 3C were 82.1, 82.1 and 85.4 me. per 100 g. on an oven-dry basis.

The rate of release of $NH_4$ was highest from the finely

Figure 11. Effect of particle size on the amount of $NH_4$ removed from $NH_4$-saturated vermiculites by equilibrating 0.2 g. clay with 2 g. $NaR_1$ with continuous shaking for periods of 3 hours to 8 days.


100
80
60
40
20
0
NH4 REMOVED (%)
0
2
4
6
8
TIME OF CONTACT (DAYS)
VERMICULITE NO. 2C ( < 0.25 mm.)
VERMICULITE NO. 2B (UNSORTED)
VERMICULITE NO. 3C ( > 0.5 mm. < 1mm.)

divided material (2C) and slowest for the coarse sample (3C). Maximum release was reached after 2 days for vermiculite 2C and not until about 6 days for 3C. Despite the difference in rate, however, the percentage removed was the same for the three samples at equilibrium. Sample 2B, with a range of particle sizes, including material found in both 2C and 3C, was simply intermediate between the two sorted vermiculites, with a rapid initial rate of release due to the small particles and a slow release thereafter from the coarse material. These results therefore show that the rate of release is a function of particle size, but the percentage removed is independent of the degree of subdivision, at least over the limited range studied. The inference is that, whatever is causing the failure to achieve maximum removal (about 98 percent for this vermiculite resin mixture), operates independently of particle size. All the evidence available from salt and resin extractions indicates that the factor preventing theoretical maximum removal is the blocking effect due to the presence of replaced $NH_4$ in the solution phase. The data in figure 11 would therefore indicate that the blocking effect of $NH_4$ in solution is independent of particle size insofar as percentage removal is concerned. In terms of the amount of $NH_4$ removed, however, there was a small difference in the blocking effects observed with vermiculite 2B and 3C.

Further investigations into the influence of particle size were made using 3 size fractions prepared from the same $NH_4$-

saturated vermiculite sample (3C). A portion of 3C that had been ground in an agate mortar to pass through a 300 mesh (< 50 micron) screen was designated as 3C''. Sample 3C' was prepared by grinding a portion of 3C to pass a 100 micron, but not a 250 micron, screen. In the preparation of 3C' a small amount of fine material was lost through the 250 micron screen. Otherwise these 3 samples were very similar except for particle size and small changes in total $NH_4$ that occurred as a result of loss of $NH_3$ during the grinding process.

The determinations made on the 3 samples include total $NH_4$ by Kjeldahl analysis (me. per 100 g. oven-dry clay), and percentage $NH_4$ removed by distilling 0.2 g. samples in 350 ml. of 1 N KOH for 2 hours and by equilibrating 0.2 g. samples of the clays for 4 days at 25°C with 20 ml. 1 N KCl, 1 N NaCl and 1 N NaCl + 0.4 me. K as KCl. In the case of the NaCl extractions with added K the vermiculite samples were extracted for a second 4-day period with fresh solution. The results are presented in table 9.

The increase in $NH_4$ removed by KOH with decreasing particle size evident in table 9 was also found by Barshad (1954b). There was also a small increase in the exchangeable $NH_4$ determined by KCl extraction. Both of these increases reflect the increase in the amount of $NH_4$ on edge sites due to the grinding. The increases in percentage removal by the K reagents were not, however, proportional to the increase in peripheral area, probably because grinding also exposed edge sites occupied by K

Table 9. Comparison of the amount of $NH_4$ removed from $NH_4$-saturated vermiculite samples that differ in particle size

| Sample | Particle size mm. | Total $NH_4$ me./100 g. | KOH distillation % | Salt extractions | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1 N KCl % | 1 N NaCl % | 1 N NaCl + 0.4 me. K ext. 1, % | ext. 2, % |
| 3C | >0.5<1 | 85.4 | 2.6 | 7.3 | 71.2 | 63.7 | 26.7 |
| 3C' | >0.1<0.25 | 83.4 | 3.0 | 7.9 | 72.1 | 63.3 | 27.6 |
| 3C'' | <0.05 | 82.5 | 5.0 | 8.5 | 63.8 | 53.8 | 21.3 |

and Mg rather than $NH_4$ since the material was a vermiculite-biotite mixture. The large decrease in the amount of $NH_4$ removed by NaCl that occurred when the vermiculite was ground to $<50$ micron size was probably also the result of exposure of K by grinding. Some of this K would be replaced by Na ions and the replaced K in solution would then have blocked further replacement of $NH_4$ and K. That is, the effect of increased accessibility of $NH_4$ ions was countered by an increase in the number of K ions in solution to block release of the interlayer $NH_4$ in the finely ground materials. The addition of 0.4 me. of K to the 20 ml. of NaCl solution lowered the recovery of $NH_4$ from samples 3C and 3C' about as much as grinding did with 3C'', indicating that it would take approximately this much K in solution to account for this decrease in recovery of $NH_4$ from 3C'' following grinding. The addition of K decreased the amount of $NH_4$ extracted from all of the samples, but the percentage difference in the recoveries by NaCl and NaCl + KCl respectively is almost the same for samples 3C' and 3C''.

The fact that a second 4 day extraction of the samples with NaCl + KCl solution increased the recovery of $NH_4$ from all of the samples means that part of the incomplete recovery of the $NH_4$ in the vermiculites by the first extraction with 1 N NaCl + KCl was due to blocking from the replaced $NH_4$. The amount of $NH_4$ removed by the second extraction with NaCl + KCl was, again, less in the case of 3C''. This could be a carry over from the extra blocking effect of the replaced K in the first extraction

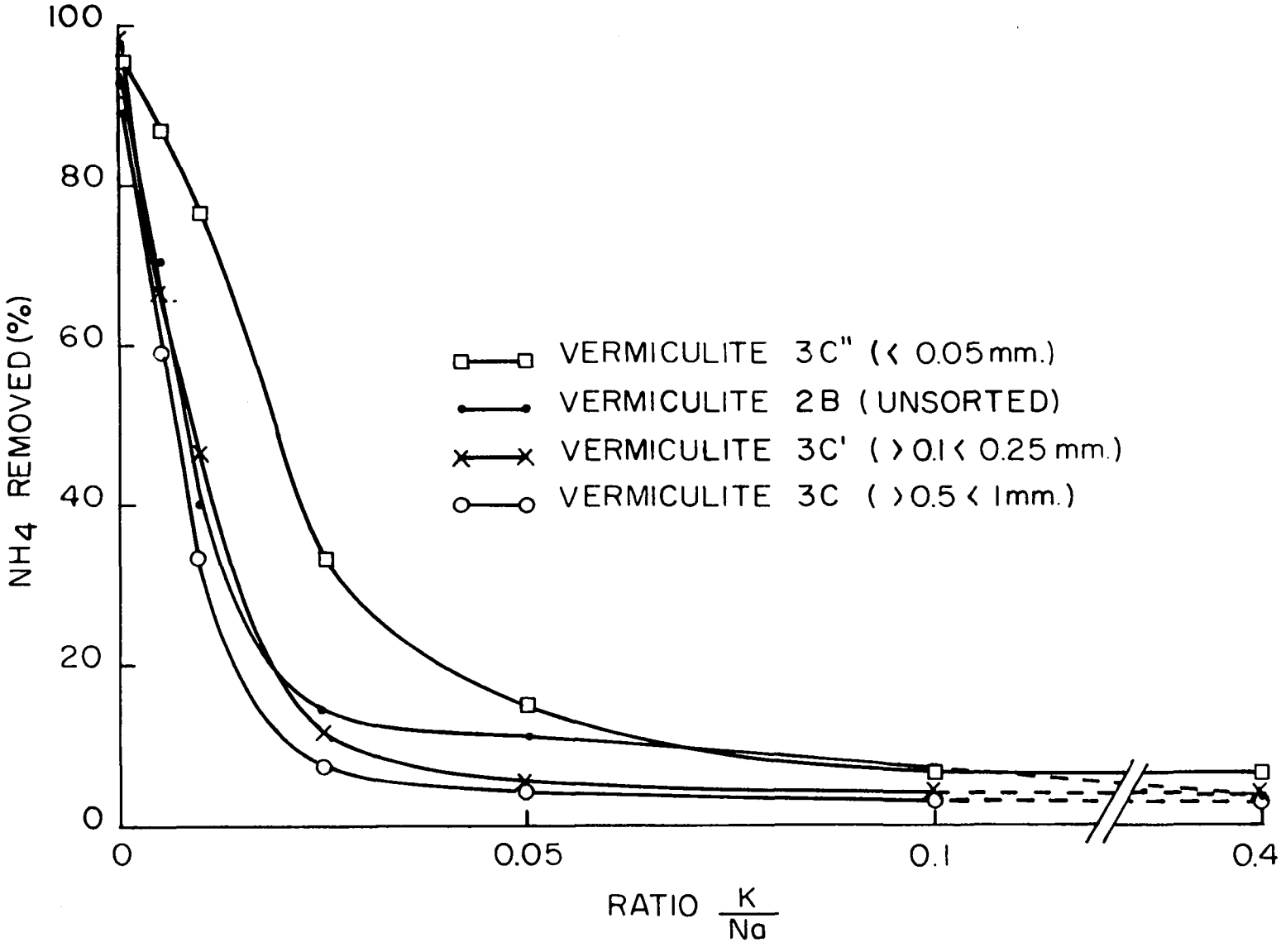
because it appears that this blocking is the result of adsorption of K on the lattice, presumably at the edge of the layers where the $NH_4$ is located. Once adsorbed, another extraction with NaCl containing K would not remove this K already on the outermost interlayer exchange sites.

Additions of K as dry KCl salt were made to 0.2 g. samples of vermiculites 3C, 3C' and 3C'' prior to distillation for 1 hour in 100 ml. of 1 N NaOH, with this volume maintained by constant additions of $NH_4$-free distilled water. The percentages of $NH_4$ removed from the 3 clays as a function of the K to Na ratio in solution are plotted in figure 12, along with the results obtained in a previous similar experiment with vermiculite 2B.

In general, the coarser the clay the lower was the percentage of $NH_4$ removed for a given ratio of K to Na. The lower recovery of $NH_4$ from the finely divided 3C'' vermiculite at the 0 level of added K, as compared to recovery from the 3C' sample, again suggests the occurrence of blocking from K released by the finely ground material.

In the absence of $NH_4$ blocking in the alkaline distillation, added K should have had a greater blocking effect in the alkaline than in the neutral NaCl extractions. At first glance this does not appear to have been the case when the $NH_4$ removed from samples 3C' and 3C'' by NaCl (table 9) is compared with the relative recoveries from the same samples by NaOH distillations without added K. However, in the NaCl extractions sufficient

Figure 12. $NH_4$ removed from $NH_4$-saturated vermiculite samples of varying particle sizes by distilling 0.2 g. of clay in 100 ml. 1 N NaOH for 1 hour as a function of the ratio of K to Na in solution.


100
80
60
40
20
0
NH4 REMOVED (%)
VERMICULITE 3C'' (< 0.05 mm.)
VERMICULITE 2B (UNSORTED)
VERMICULITE 3C' (> 0.1 < 0.25 mm.)
VERMICULITE 3C (> 0.5 < 1mm.)
0
0.05
0.1
0.4
RATIO K/Na

time was allowed for the amount of $NH_4$ removed to be determined only by the blocking by $NH_4$ and K in solution. The NaOH distillation, on the other hand, lasted only 1 hour. Thus, the amounts of $NH_4$ removed by this technique reflect differences in rate of removal of $NH_4$ from the various particle sizes. Therefore the differences in the NaOH distillation values cannot be used to evaluate the relative magnitude of the blocking effect of K in samples with different particle size. It is evident from figure 12, however, that added K reduced the amount of $NH_4$ replaced from each fraction and that the maximum degree of blocking from high levels of added K decreased as the particle size decreased.

Since the foregoing data suggested the presence of K in sample 3C'' which was accessible for replacement, a portion of this material was leached with $NH_4Cl$ to remove this K. The leached sample was then washed with ethanol and air dried to give sample 3C'''. A comparison between the samples 3C'' and 3C''' in terms of total $NH_4$ (Kjeldahl analysis), exchangeable $NH_4$ (KOH distillation) and the effect of K blocking on the amount of $NH_4$ removed by distilling 0.2 g. vermiculite in 100 me. 1 N NaOH for 1 hour is given in table 10.

Leaching the ground $NH_4$-saturated vermiculite 3C'' with $NH_4Cl$ resulted in a marked increase in the total amount of $NH_4$ adsorbed, and also in the amount released to KOH. The total amount of $NH_4$ (me. per 100 g.) fixed against KOH was increased in the leached 3C''' sample to a level above that found in any

Table 10. The effect of leaching $NH_4$-vermiculite sample 3C'' (< 50 micron) with $NH_4Cl$ on the total $NH_4$ absorbed and the replaceability of this $NH_4$

| Treatment | $NH_4$ removed, me. per 100 g. oven-dry clay | | | |
|---|---|---|---|---|
| | 3C'' | | 3C''' | |
| | me. | % | me. | % |
| Kjeldahl | 82.5 | 100.0 | 108.0 | 100.0 |
| KOH distillation | 4.1 | 5.0 | 17.3 | 16.1 |
| NaOH distillation 0 me. K | 79.1 | 95.9 | 105.4 | 97.6 |
| NaOH distillation 0.5 me. K | 71.9 | 87.2 | 90.9 | 84.2 |
| NaOH distillation 1.0 me. K | 63.0 | 76.4 | 83.6 | 77.4 |
| NaOH distillation 2.5 me. K | 27.5 | 33.3 | 51.3 | 47.6 |

of the other samples (3C, 3C', 3C''), but on a percentage basis there was less fixed $NH_4$ in 3C''' than in 3C''. This is what Barshad (1954b) found in his particle size studies with vermiculite. The leached sample (3C''') however, released about the same proportion of its total $NH_4$ as 3C'' when distilled in NaOH at the lower levels of added K. Therefore, it may be concluded that the blocking effect of added K is independent of both the amount of $NH_4$ on the clay and the amount of $NH_4$ removed, but is related to the percentage removed.

Based on the results of the resin extractions of $NH_4$-vermiculites, it can be said that, although the rate of removal of

$NH_4$ increases with decreasing particle size, the percentage removal is not affected. The increase in the number of edge exchange sites leads to an increase in the amount removed by K salts and KOH, that is, in the amount of exchangeable $NH_4$. Where both the K and $NH_4$ released from the mineral itself can accumulate in solution, as in a NaCl extraction, there is a decrease in the amount of $NH_4$ removed as particle size decreases. In a distillation in NaOH, on the other hand, with the $NH_4$ constantly being removed from solution, the rate of removal of interlayer $NH_4$ is more rapid from the finer particles, and a greater proportion of the $NH_4$ present is removed in 1 hour at a given ratio of K to Na ions in solution. Again, the presence of the $NH_4$ ion in solution would seem to be more important than the level of K in reducing the percentage of $NH_4$ removed from vermiculite. It would appear that blocking is independent of particle size if side effects, such as those due to release of K on grinding, are removed.

## Temperature of Extraction

An 8 hour boiling extraction in flasks fitted with reflux condensers using 1 g. of vermiculite 2B in 100 ml. of 1 N NaCl removed approximately 47 me. $NH_4$ per 100 g. out of the total of 82 present in the clay. In salt extractions at room temperature, however, it was found that an 8 day treatment using the same clay and the same ratio of clay to NaCl removed about 67 me. of $NH_4$ per 100 g. of oven-dry clay. Allison and Roller (1955)

attributed the greater efficiency of KCl compared to KOH in the extraction of $NH_4$ from soils to fixation of exchangeable $NH_4$ by the soil clays at the high temperature of the boiling KOH. However, Scott, Hanway and Edwards (1958) showed that room temperature distillations of $NH_4$-saturated vermiculite in KOH removed essentially the same amount of the ammonium as the boiling technique. Increasing the temperature during extraction, therefore, appears to have a negative influence upon the amount of $NH_4$ removed from vermiculite during neutral salt extractions, and little or no effect upon the results of a KOH distillation. Conversely, increasing the temperature at which soils containing vermiculite were incubated following additions of $NH_4$ salts, increased the fixation of $NH_4$ under moist conditions in studies carried out by Nommik (1957).

To investigate in more detail the effect of temperature on the replaceability of the $NH_4$ in vermiculite, NaCl extractions were made at 4°, 25°, 50°, 75° and 100°C. Resin treatments at 4°, 25° and 100°C temperatures were also investigated. The samples that were extracted at 4° and 25°C were continuously agitated on wrist action shakers in constant temperature rooms. At the higher temperatures, the samples and extracting solutions were placed in 100 ml. polypropylene centrifuge tubes which were subsequently fitted with reflux condensers prior to incubation of the samples in a water bath. Agitation at the higher temperatures was confined to swirling the centrifuge tubes at irregular intervals after it had been demonstrated that more

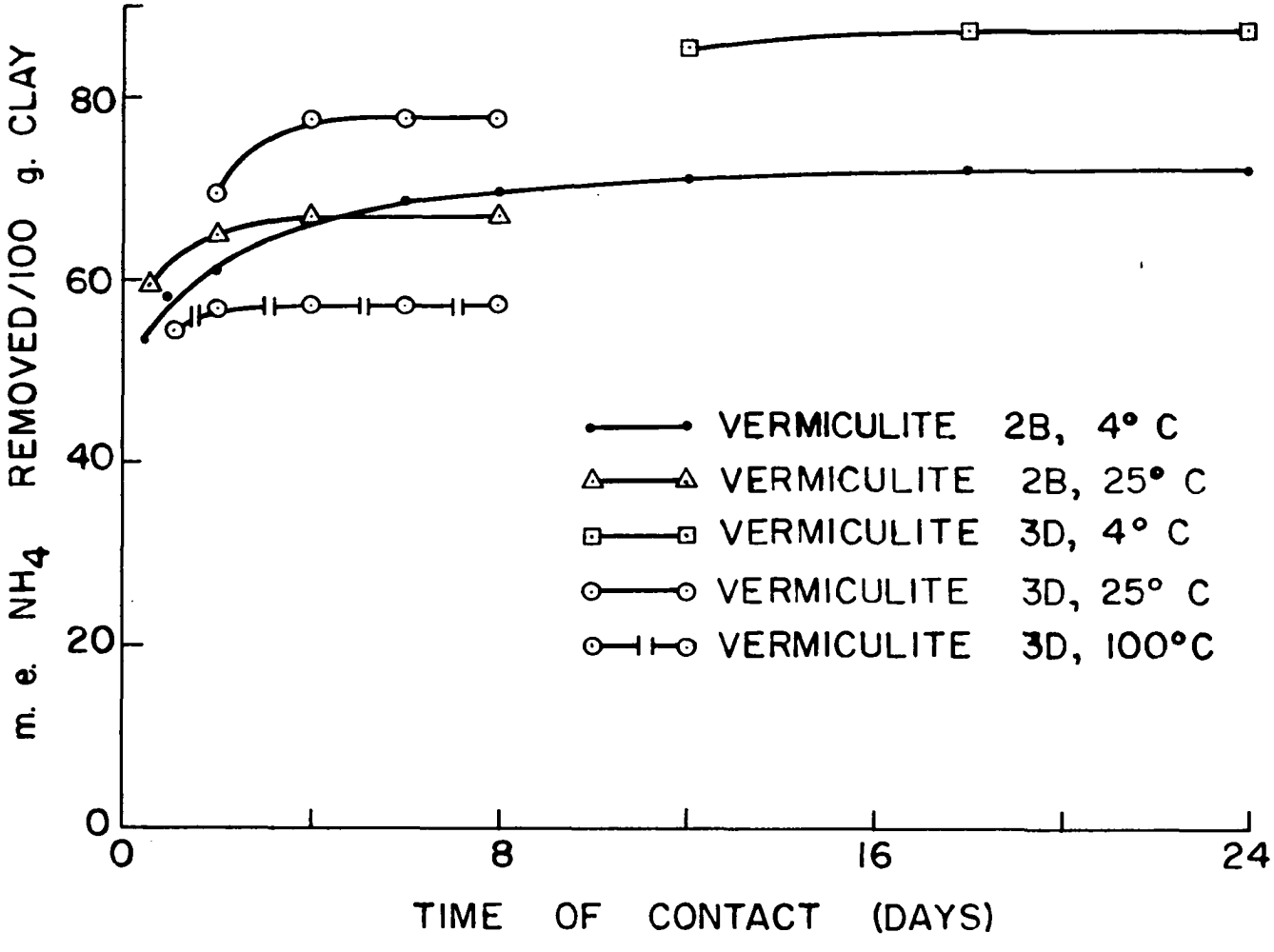
vigorous and frequent agitation by means of glass paddles inserted through the condensers gave the same results.

To determine the influence of temperature upon the time required to reach equilibrium, studies on the rates of removal of $NH_4$ from vermiculite were initiated first. Samples of vermiculite 2B (0.2 g.) and 3D (0.1 g.) were treated with 20 ml. of 1 N NaCl and the $NH_4$ in solution determined after various times of contact between clay and extractant. The results for the 4° and 25°C temperatures are plotted for the resin, and the 4°, 25° and 100°C values for the NaCl extractions. The results are shown in figure 13.

There was no further removal of $NH_4$ from either vermiculite 2B or 3D beyond 18 days of contact at the 4°C temperature. Similar results were obtained when vermiculite 2B was extracted with $NaR_o$ (experiment described later). Therefore, 18 days was adopted for subsequent extractions at 4°C. As previously decided, an 8 day period was used for NaCl and Na-saturated resin extractions at 25°C. No increase in the amount of $NH_4$ removed was observed with either clay by increasing the contact period from 4 to 6 days at 100°C. Likewise, the 6 day values for the amount of $NH_4$ removed from both vermiculites at 50°C and 75°C were the same as those for 8 days of contact, leading to the adoption of a 6 day period of equilibration at these intermediate temperatures.

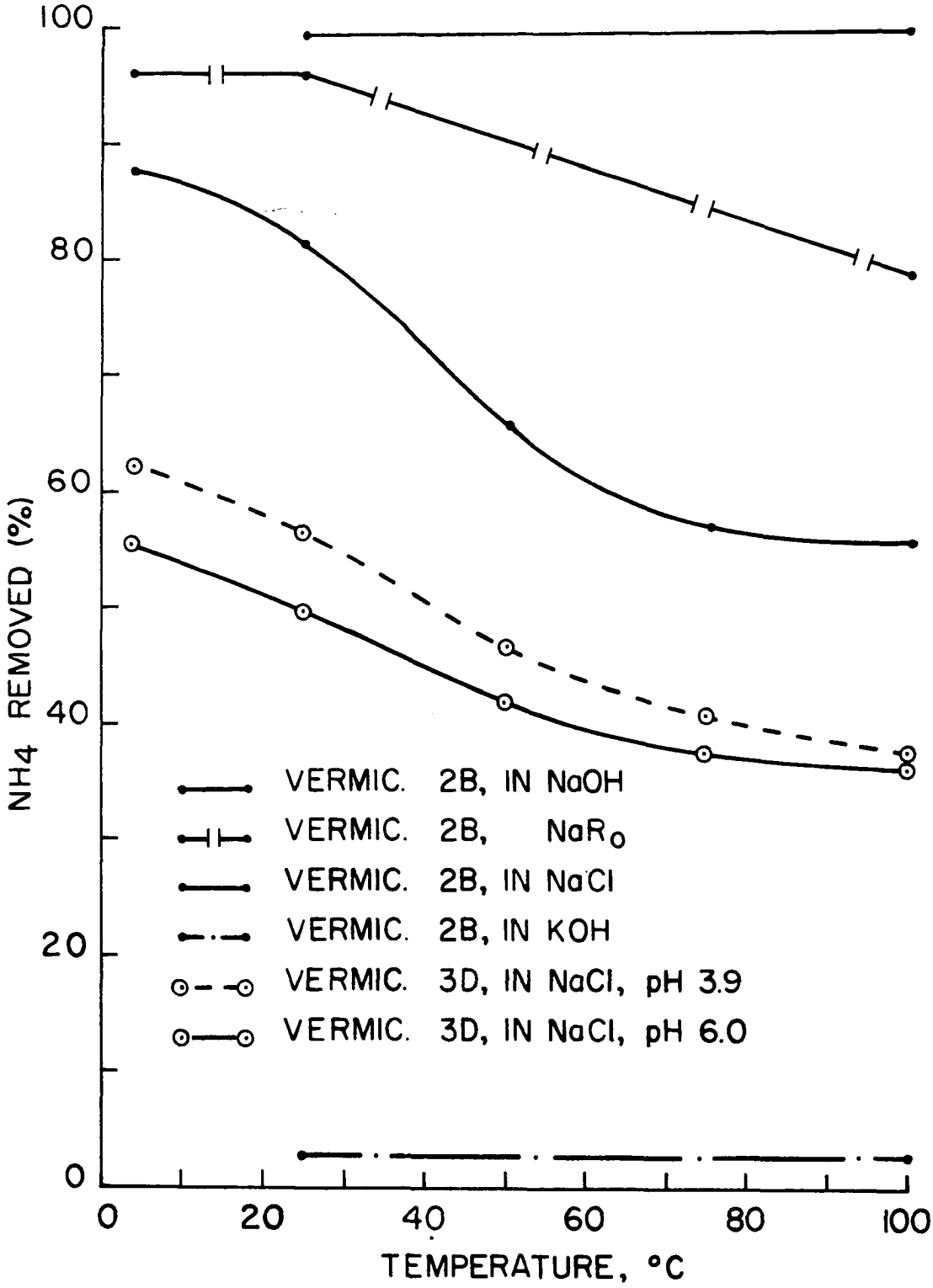
Using the methods described in the preceding paragraphs, the maximum amounts of $NH_4$ removed by NaCl (pH 6.0) from

Figure 13. $NH_4$ removed from $NH_4$-saturated vermiculites 2B and 3D by equilibrating 0.2 and 0.1 g. samples respectively, with 20 ml. 1 N NaCl at various temperatures as affected by time of contact.


m. e. $NH_4$ REMOVED/100 g. CLAY
0
20
40
60
80
0
8
16
24
TIME OF CONTACT (DAYS)
VERMICULITE 2B, 4° C
VERMICULITE 2B, 25° C
VERMICULITE 3D, 4° C
VERMICULITE 3D, 25° C
VERMICULITE 3D, 100°C

vermiculites 2B and 3D were determined at 5 temperatures (4°, 25°, 50°, 75° and 100°C) in order to establish the relationship between replaceability of $NH_4$ in vermiculite and the temperature of equilibration. Vermiculite 3D was also treated with 1 N NaCl adjusted with HCl to pH 3.9 to ensure that no $NH_4$ would be lost from the system and to investigate in a limited way the relationship between the amount of $NH_4$ removed from this degraded vermiculite, the pH of the extracting solution and the temperature at which the comparison was made. The amount of $NH_4$ which could be removed from vermiculite 2B by $NaR_o$ was also determined at 3 temperatures (4°, 25° and 100°C) in order to give the comparison of temperature effects between salt and resin extractions. For the above determinations, 0.2 g. and 0.1 g. samples of vermiculites 2B and 3D, respectively, were treated with 20 me. Na as NaCl or $NaR_o$ in 20 ml. of $H_2O$. For comparison purposes the results of room temperature and boiling distillation of vermiculite 2B in 1 N KOH and 1 N NaOH were also determined. For the boiling alkaline distillation 0.2 g. samples of vermiculite 2B were boiled for 2 hours in 350 ml. of 1 N KOH and NaOH and $NH_4$-free distilled water was added continuously through a separatory funnel to maintain constant volume. The room temperature distillations (5 days) were carried out in modified Conway micro-diffusion cells using 0.07 g. of clay and 7 ml. of 1 N KOH and 0.04 g. of vermiculite and 4 ml. of 1 N NaOH. The results of the salt and resin extractions are plotted in figure 14 as percentages of the total $NH_4$

Figure 14. $NH_4$ removed from $NH_4$-saturated vermiculite 2B by NaCl, $NaR_o$, NaOH and KOH and from $NH_4$-saturated vermiculite 3D by NaCl at 2 pH levels, as affected by temperature.


100
80
60
40
20
0
NH4 REMOVED (%)
0
20
40
60
80
100
TEMPERATURE, °C
VERMIC. 2B, IN NaOH
VERMIC. 2B, NaR0
VERMIC. 2B, IN NaCl
VERMIC. 2B, IN KOH
VERMIC. 3D, IN NaCl, pH 3.9
VERMIC. 3D, IN NaCl, pH 6.0

removed. Vermiculite 2B and 3D contained 82.1 and 157.7 me. of $NH_4$ per 100 g. of oven-dry clay, respectively.

Distillations in KOH and NaOH to remove the $NH_4$ from vermiculite 2B showed no sensitivity to temperature. The amounts of $NH_4$ removed from both vermiculites by NaCl, on the other hand, were sharply reduced as temperature increased, especially over the range from 25° to 50°C and especially in the case of vermiculite 2B. The resin $NaR_o$ was also less efficient at the higher temperature in removing $NH_4$ from vermiculite 2B, although there was little difference between the 4° and 25°C values. Since the amount of $NH_4$ removed from vermiculite 2B by the resin at 25°C represents a high proportion of the total present, the failure to achieve higher recovery at 4°C is no doubt due to the fact that maximum possible removal has already been reached at the higher temperatures.

The possibility that the lower recoveries in NaCl (pH 6.0) at the higher temperatures were due to losses of gaseous $NH_3$ can be discounted because the total $NH_4$ in the clays after extraction was determined a number of times, and practically all of the $NH_4$ was accounted for. Also, in several 100°C extractions with NaCl (pH 6.0) the tops of the condensers were connected to boric acid traps. It was observed that the pH of the NaCl solution added to vermiculite 2B increased from 6 to over 7 after several days of shaking. Since K-micas have been shown by Garrels and Howard (1959) to react with water to give an alkaline reaction, the selective uptake of very small amounts

of H ions from solutions which they postulate is probably occurring also with the $NH_4$-saturated vermiculite. The increase in pH, however, was apparently not sufficient to lead to a loss of $NH_4$ as $NH_3$.

The reasons for the negative effect of temperature on the removal of $NH_4$ from $NH_4$-saturated vermiculite by NaCl and $NaR_o$ were not immediately apparent. The possibility that a decreasing degree of hydration of the Na ions at the higher temperature was involved was considered to merit some attention.

## Solvents and Anions

Cations between the layers of a contracted lattice are physically inaccessible for exchange. To remove such cations therefore, requires replacing ions which are large or hydrated so that the lattice will be expanded following their adsorption. Successive replacement of fixed cations, starting from the outside edges, therefore makes accessible those cations still further within the contracted lattice.

Solutions of salts in methanol have been used in base exchange studies with clays and soils. Bower and Truog (1941) obtained higher values for cation exchange capacity when divalent cations rather than monovalent were used in aqueous solution. Dissolving the divalent salts in 99 percent methanol brought the values for cation exchange capacity to the level of the determinations made using monovalent salts dissolved in water. This the authors attributed to the absence, in the

alcohol solutions, of what they termed "basic exchange salts" such as $(MgOH)^+$ which were apparently being absorbed as monovalent cations from water solutions of salts having divalent cations. Changes in the relative replacing power of cations with increasing proportions of alcohol in the solvent have been explained on the basis of reductions in the degree of hydration of the cations in solution. However Kelley (1948) questions the assumption that cation hydration alone was involved, adding that the activity of the ions dissolved in alcohol may also have been changed.

It was decided to investigate the effect of using Na salts dissolved in alcohol and alcohol water mixtures on the amount of $NH_4$ removed from $NH_4$-saturated vermiculite. Samples of vermiculite 2B (0.2 g.) were equilibrated for 8 days at 25°C in 20 ml. of 1 N $NaC_7H_5O_3$ in water and in mixtures of water and ethanol containing 70 and 90 percent of the alcohol. Solutions 0.2 N in $NaC_7H_5O_3$ dissolved in water and absolute ethanol were also used to extract $NH_4$ from the vermiculite, and 1 N NaCl in water and 50 percent ethanol were likewise used as extractants. The results are presented in table 11 expressed both as me. $NH_4$ removed per 100 g. of oven-dry clay and as the percentage of the total $NH_4$ removed.

The $NH_4$ removed from the vermiculite by 1 N solutions of both NaCl and $NaC_7H_5O_3$ was reduced by adding alcohol, and, in the case of the $NaC_7H_5O_3$, the recovery decreased as the proportion of alcohol increased. The 0.2 N solution of $NaC_7H_5O_3$ in

Table 11. $NH_4$ removed from $NH_4$-vermiculite 2B by NaCl and $NaC_7H_5O_3$ as affected by the amount of ethanol in the solvent

| Extractant | | $NH_4$ Removed | |
|---|---|---|---|
| Salt | Solvent | me./100 g. | % |
| 1 N NaCl | $H_2O$ | 66.6 | 81.1 |
| " | 50% $C_2H_5OH$ | 58.8 | 71.7 |
| 1 N $NaC_7H_5O_3$ | $H_2O$ | 69.3 | 84.4 |
| " | 70% $C_2H_5OH$ | 44.5 | 54.2 |
| " | 90% $C_2H_5OH$ | 21.0 | 25.6 |
| 0.2 N $NaC_7H_5O_3$ | $H_2O$ | 33.9 | 41.3 |
| " | abs. $C_2H_5OH$ | 0.9 | 1.1 |
| 0.2 N KCl | $H_2O$ | 8.3 | 10.1 |

absolute ethanol removed only about 1 percent of the $NH_4$ present in the vermiculite, but at the same concentration in water the salt displaced over 40 percent of the $NH_4$. Since 0.2 N KCl displaced 10 percent of the $NH_4$, most of this must have come from interlayer positions if the "unhydrated" Na ions in the absolute alcohol are displacing all of the $NH_4$ on the crystal edges. However, the degree of dissociation of electrolytes in solution is directly related to the polarity of the solvent. It is impossible, therefore, to separate out ionic hydration effects, if present, from those related to the degree of dissociation of the NaCl and $NaC_7H_5O_3$. However, if ion activities are much

reduced in alcohol as opposed to water, it is difficult to explain the results of the base exchange studies of Bower and Truog (1941).

Glycine is an amino acid which is dipolar in nature. When glycine is dissolved in water, there is a steady increase in the dielectric constant of the solution as the concentration of glycine is increased. To see whether an increase in the polar nature of the solvent molecules would affect the amount of $NH_4$ removed by Na ions, solutions 1 N in NaCl were also made 0.00, 0.08, 0.4, 1.0 and 2.5 M in glycine for use in vermiculite extractions.

Samples of vermiculite 2B (0.2 g.) were equilibrated at 25°C with 20 ml. of the 1 N NaCl solutions with and without added glycine. The amounts of $NH_4$ removed, expressed as me. per 100 g. of oven-dry clay and as percentages of the total, are given in table 12.

The glycine had little effect on the amount of $NH_4$ displaced by 1 N NaCl as long as its concentration was low. At the two higher concentrations, however, the amino acid interfered with the removal of $NH_4$. Walker (1950) has shown that vermiculite is capable of forming 2 kinds of organic complexes, one due to a cation exchange reaction and the other due to interlamellar adsorption of complete molecules. Amino acids could form both types, since they dissociate to yield a relatively large cation. Therefore the decrease in $NH_4$ removal observed when glycine was added could have been due to the

Table 12. The effect of adding glycine to NaCl solutions upon the recovery of the $NH_4$ in vermiculite 2B

| Extractant | | Extraction time in days | $NH_4$ Removed | |
|---|---|---|---|---|
| NaCl | Glycine | | me. | % |
| 1 N | 0.00 M | 8 | 66.6 | 81.1 |
| 1 N | 0.08 M | 4 | 66.9 | 81.6 |
| 1 N | 0.4 M | 5 | 66.5 | 81.0 |
| 1 N | 1.0 M | 4 | 59.4 | 72.4 |
| 1 N | 2.5 M | 4 | 43.9 | 53.5 |

clogging effect of adsorbed glycine, or to the fact that some of the Na ions were simply being tied up as Na-glycinate.

Chloride salts were used throughout most of the studies on the replaceability of $NH_4$ in vermiculite. One reason for the choice was the fact that NaCl can be obtained relatively free of $NH_4$ and K. Another reason of some potential importance in soils is the fact that the chloride anion is about the only one which can be used if interference from dissolution of organic compounds is to minimized. The use of 1 N $NaC_7H_5O_3$ in water in the previous experiment gave a slightly higher recovery of $NH_4$ in 8 days than 1 N NaCl (table 12). A 1 N $NaH_2PO_4$ buffer (pH 6.5) removed 64.9 me. of $NH_4$ per 100 g. from vermiculite 2B in 24 hours compared to 64.2 me. of NaCl (pH6) under the same conditions. Although citrate and acetate buffers were used at various times in the vermiculite studies, no data were obtained

with them under conditions that were exactly comparable to the NaCl extractions. However, changing the soluble anion associated with Na appears to have little influence, at room temperature, on the amount of $NH_4$ removed from $NH_4$-saturated vermiculite.

## Effect of Degradation

As previously noted, the Montana vermiculite used throughout the current study was a portion of the same material investigated by Allison, Roller and Doetsch (1953). According to Barshad (1948) this sample is a high exchange capacity material consisting of a relatively pure vermiculite mixed with interleaved vermiculite-biotite.

Barshad (1948) was able to partially convert this same mixed vermiculite-biotite material into vermiculite by leaching with 1 N $MgCl_2$ for an extended period and into biotite by leaching with KCl. It has recently been shown by Scott, Hunziker and Hanway (1960) that the addition of sodium tetraphenylboron (hereafter designated as $NaBPh_4$) to concentrated salt solutions increased the efficiency with which the salts removed K from micaceous minerals. The $NaBPh_4$, by precipitating the K as rapidly as it is removed from the lattice, prevents the blocking of further K removal and the reversion of displaced K back to interlayer exchange sites. Since the $NH_4$ ion will not displace K from biotite, it is impossible to convert this vermiculite-biotite mixture by treating it directly with $NH_4$ salts.

Much of the K in the biotite can be extracted, however, by treating the material with a mixture of NaCl and $NaBPh_4$. This treatment converts the minerals to the Na form, and the material can then be treated with $NH_4$ salt to substitute $NH_4$ for Na. This procedure, described in some detail under "Methods and Materials" for illite, was used in preparing an $NH_4$-saturated sample of degraded vermiculite which was designated as 3D. This sample was prepared to study the effect of this degradation procedure on the properties of the vermiculite, and in particular to determine if the fixation and release of the $NH_4$ in the degraded material was the same as in the natural vermiculite.

The first determinations made on the degraded and undegraded vermiculites 3C and 3B, respectively, were analysis for total $NH_4$ and total K to evaluate the effect of degradation on the charge density and the total $NH_4$ adsorption possible. The actual procedures used are described under "Methods and Materials". The results expressed as me. $NH_4$ per 100 g. of oven-dry clay, are given in table 13.

The decrease of 5.8 me. in the total $NH_4$ + K in the degraded sample does not necessarily indicate that a decrease in charge density has occurred. No measurements were made of the Mg and Ca that could have been trapped on interlayer exchange sites in sample 3B, nor was the trapped Na determined in the degraded sample (3D). The fact that the decrease in total K upon degradation was almost matched by the increase in $NH_4$ suggests that the expansion and re-collapse of the biotite lattice,

Table 13. Total $NH_4$ and K contents of comparable degraded (3C) and undegraded (3B) $NH_4$-saturated vermiculites

| Sample | Total $NH_4$ me./100 g. | Total K me./100 g. | $NH_4$ + K me./100 g. |
|---|---|---|---|
| 3B | 85.8 | 85.6 | 171.4 |
| 3D | 157.7 | 7.9 | 165.6 |
| Difference | 71.9 | 77.7 | 5.8 |

at least of the type present in this vermiculite-biotite mixture, can be accomplished with little or no damage to the so-called non-expanding mica structure.

To determine the effect of degradation upon the replaceability of the ammonium substituted for K on the exchange, several extraction procedures were compared on vermiculites 3D (degraded) and 2B (undegraded). The $NH_4$ removed by treating 0.2 and 0.1 g. samples of 2B and 3D, respectively, with 20 me. of Na as NaCl and $NaR_1$ and with 20 me. of K as KCl, for 8 days, was determined. The smaller weight of clay was used in the case of vermiculite 3D in order to approximately equate the total amount of $NH_4$ in the samples. Distillations in 1 N KOH were also carried out by boiling the same amounts of the 2 vermiculites in 350 ml. of solution for 2 hours. The amounts of $NH_4$ removed by the various treatments are given in table 14 as me. per 100 g. of oven-dry clay and as percentages of the total originally present.

Table 14. The effect of degrading Montana vermiculite prior to $NH_4$ saturation on $NH_4$ release in various extracting solutions

| Vermiculite sample | $NH_4$ removed | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | KOH | | KCl | | NaCl | | $NaR_1$ | |
| | me./100g. | % | me./100g. | % | me./100g. | % | me./100g. | % |
| 2B | 2.8 | 3.3 | 8.9 | 10.8 | 67.2 | 81.9 | 81.1 | 98.8 |
| 3D | 5.2 | 3.3 | 7.1 | 4.5 | 77.6 | 49.2 | 154.1 | 97.7 |

There was little difference between the percentages of $NH_4$ removed by $NaR_1$ from the two clays. However, the proportion of the $NH_4$ which was extractable by 1 N NaCl was much lower in the case of the degraded sample. It would therefore appear at first glance that the two clays have reacted differently to accumulations of replaced $NH_4$ in solution.

The NaCl solution removed only 49 percent of the total $NH_4$ in sample 3D compared to almost 82 percent of the $NH_4$ in vermiculite 2B. In terms of absolute concentrations of $NH_4$ in solution at equilibrium 0.078 and 0.134 me. were present in the 20 ml. of 1 N NaCl with vermiculites 3D and 2B respectively. It should be noted, however, that only 0.1 g. of sample 3D was used compared to 0.2 g. of 2B. Thus, the amounts of $NH_4$ in solution per unit weight of clay were very similar in both extractions. Hanway (1954) found the same relationship to apply when different amounts of the same vermiculite samples were extracted with 1 N NaCl. Therefore the $NH_4$ in solution at

equilibrium appears to be determined by the amount of clay present as well as by the ratio of $NH_4$ to Na in solution.

Similarly, the amount of $NH_4$ removed by KCl seems to indicate that only a certain amount of $NH_4$ per unit weight of clay can be present in the solution phase with this salt also. On this basis, a clay which contained only a small amount of fixed $NH_4$ near the crystal edges could conceivably release it all to a KCl solution equally as well as to NaCl if comparable ratios of cation to clay were used.

The percentage of the $NH_4$ removed by KOH, on the other hand, appeared to be insensitive to the amount of clay present. With the $NH_4$ being constantly removed, only a very small but definite proportion of the total $NH_4$ in the clay was displaced. Hanway (1954) also found that the proportion of the $NH_4$ in vermiculite removed by distilling in NaOH-KCl mixtures was constant regardless of the clay to solution ratio.

On the basis of the results presented it would appear that there is no real difference between the replaceability of the $NH_4$ adsorbed on sites in vermiculite previously occupied by Mg and Ca and the $NH_4$ adsorbed on sites previously occupied by K. The cation exchange resin used extracted the $NH_4$ from both materials with equal facility. However, if the displaced $NH_4$ is allowed to accumulate in solution, the amount of $NH_4$ removed from vermiculites similar in particle size is proportional to the amount of clay present. This means that, for vermiculite samples of equal weight extracted with the same volume of NaCl,

the salt solution will be less efficient in removing ammonium from the sample with the higher proportion of its exchange sites occupied by $NH_4$. Distillation in KOH, on the other hand, removes a rather fixed proportion of the total $NH_4$ present in vermiculite, irrespective of the amount of clay in a given volume of solution, or of the degree of $NH_4$ saturation.

## DISPLACEMENT OF AMMONIUM FROM ILLITE

Soil illite, although a poorly defined mineral group at present, is generally considered to be largely dioctahedral. As reflected in such properties as charge density, K content and location of the negative charge due to isomorphous substitution, this material is somewhere between well crystallized muscovite mica on the one hand and montmorillonites on the other. The proven ability of soil illite to fix $NH_4$ and K makes a comparison between dioctahedral illite and trioctahedral vermiculite, with respect to the replacement of adsorbed $NH_4$, of considerable interest.

Illite is found in relatively high concentrations in shales and underclays of marine origin. Normally the illite from such deposits has a higher K content than soil illite and a lower exchange capacity. These illitic materials are readily available and contain, compared with the clays extracted from soils, relatively little extraneous matter. Therefore they are very useful in studying the behaviour of similar materials found in soils. In the case of $NH_4$ fixation, however, the effect of K removal must be included to make the illites from natural deposits more comparable to soil illites in K content and $NH_4$ fixing capacity. There are 2 major sources of illite from natural deposits, namely Fithian illite from deposits near the town of the same name in Illinois, and Grundite, found near Morris, Illinois. In this investigation of the fixation and

release of $NH_4$ by illite only the Grundite-illite was used.

## Effect of Various Treatments on $NH_4$ Adsorption and Fixation by Illite

When Grundite-illite is $NH_4$-saturated directly, very little fixation occurs. Also, this illitic material contains nitrogen, which complicates any studies of $NH_4$ fixation. Therefore, before the illite samples listed in table 2 were prepared for studies on the replaceability of fixed $NH_4$, several preliminary experiments were carried out on methods of obtaining appreciable fixation in the illite used. These experiments were primarily concerned with the effect of removing K. It is evident from the literature, however, that illite will fix more $NH_4$ if the clay is dried at about 110°C in the $NH_4$-saturated state. Therefore the effect of drying was also investigated.

Several small samples of degraded and undegraded illite were prepared from the 1952 batch of Goose Lake Grundite. The method of degradation was similar to that described for illite 2C in the "Methods and Materials" section, but some samples were left in the Na-saturated state following degradation. In addition, the various samples were dried to different degrees as follows:

Sample a. Na-saturated < 2 micron degraded illite dried at 110°C.

Sample b. $NH_4$-saturated < 2 micron degraded illite dried at 110°C.

Sample c. $NH_4$-saturated < 2 micron degraded illite kept moist (200% $H_2O$).

Sample d. Na-saturated < 2 micron undegraded illite dried at 110°C.

Sample e. $NH_4$-saturated < 2 micron undegraded illite dried at 110°C.

Sample f. $NH_4$-saturated < 2 micron undegraded illite kept moist (200% $H_2O$).

The total nitrogen in these samples was determined by Kjeldahl analysis, and the nitrogen removed by distilling 0.5 g. of clay in 350 ml. of 1 N KOH for 1 hour was also measured. The results are given as me. $NH_4$ per 100 g. of oven-dry clay in table 15. The nitrogen removed by KOH was considered to be "exchangeable $NH_4$" and the "fixed $NH_4$" values were calculated by difference even though the exact nature of the naturally occurring nitrogen in the illite was unknown.

Drying at 110°C caused a loss of nitrogen from both degraded and undegraded illites amounting to approximately 11 percent and 16 percent, respectively. Apparently some of the adsorbed $NH_4$ was lost at this temperature. Drying had little effect on the amount of fixed $NH_4$ in the undegraded samples (e, f) but a 30 percent increase in fixation occurred when the degraded $NH_4$-saturated sample (b) was dried at 110°C.

It is also evident from table 15 that sample (d), the Na-saturated natural illite, contained 6.9 me. of $NH_4$ per 100 g. of clay, as determined by an extended Kjeldahl digestion. Very little of this nitrogen was replaced by a KOH distillation, therefore it would appear as fixed $NH_4$ in the calculation of fixed $NH_4$ in the comparable $NH_4$-saturated samples. If the

Table 15. Effect of degradation and drying treatments on the total and KOH extractable nitrogen in illite samples

| Sample | Nitrogen determinations, me. $NH_4$/100 g. clay | | |
|---|---|---|---|
| | Total N (Kjeldahl) | "Exchangeable $NH_4$" (KOH) | "Fixed $NH_4$" (calculated) |
| a | 3.7 | 0.3 | 3.4 |
| b | 86.1 | 26.9 | 59.2 |
| c | 96.8 | 56.8 | 40.0 |
| d | 6.9 | 0.5 | 6.4 |
| e | 28.0 | 20.6 | 7.4 |
| f | 34.4 | 26.4 | 8.0 |

values for the fixed $NH_4$ in these $NH_4$-saturated samples (e, f) are corrected for this native N, only 1 and 1.5 me. of $NH_4$ per 100 g., respectively, were fixed. Thus, the question arises as to how much of the 6.9 me. of $NH_4$ per 100 g. of illite is inorganic $NH_4$ and how much is organic N converted to $NH_4$ by Kjeldahl digestion. The degradation treatment removed 3.2 me. per 100 g. out of the 6.9 present, but some of this could have been nitrogen that was removed as organic matter in solution or suspension. Treatment of a comparable sample of illite with 1 N HCl-HF removed 4.6 me. $NH_4$ per 100 g. Total carbon determinations also indicated that about 0.9 percent of this element was present in organic form in both the natural illite and a $<50$ micron fraction sieved directly from it. It would therefore appear that the native nitrogen in the illite is partly organic,

partly inorganic fixed ammonium.

In order to avoid complications due to the presence of organic matter and to provide a clay comparable to the nitrogen-free vermiculite, techniques for removing organic matter were considered. Scott, Hanway and Stanford (1956) attributed the exothermic peak at about 400°C to the oxidation of the organic matter in the 1952 batch of Goose Lake Grundite. Since Grim and Bradley (1940) reported that no structural changes occurred in illite at heating temperatures below 800°C, it was decided to heat the illite in its natural state at 450°C for 24 hours. The data for the 450°C heated < 20 micron fraction (sample 2A in table 2) showed that the heat treatment lowered the content of native N to essentially zero. The exchange capacity of the heated clay was not affected to any great extent since the $NH_4$-saturated 450°C heated <2 micron sample 2B contained 27 me. $NH_4$ per 100 g. of clay whereas the comparable unheated material, sample e in table 15, had a total nitrogen content of 28.0 me. $NH_4$ per 100 g. of which 6.9 me. per 100 g. were present before the $NH_4$ saturation. The level of organic carbon in a < 50 micron fraction of the natural illite also fell from 0.9 to 0.07 percent when the sample was heated at 450°C.

The data in table 15 show that the degradation treatment resulted in a large increase in the amount of adsorbed, exchangeable and fixed $NH_4$ in the illite. Even if the fixed $NH_4$ values are corrected for the naturally occurring nitrogen in the illite a comparison of samples b and c shows that the increase in $NH_4$

fixation amounted to 54.8 me. $NH_4$ per 100 g. It is also evident that the degraded illite fixed appreciable amounts of $NH_4$ without drying.

On the basis of these effects from heating and drying, the No. 2 group of illite samples, described under "Materials and Methods" and used in most of the $NH_4$ release studies with illite, were heated at 450°C as the first step in their preparation, and the $NH_4$-saturated materials were dried at 110°C.

To obtain further information on the effect of the degradation treatment on the illite samples, the relationship between changes in K content and $NH_4$ adsorption was established. The total K and $NH_4$ in the 450°C heated, <20 micron, $NH_4$-saturated samples 2C and 2B (table 2) were determined by the methods described under "Analytical Procedures". These values and the amounts of $NH_4$ removed from each by a boiling distillation of 0.2 g. clay in 350 ml. of 1 N KOH are given in table 16 as me. $NH_4$ per 100 g. of oven-dry (110°C) clay.

The amounts of $NH_4$+K in the degraded and undegraded samples were almost identical. This means that $NH_4$ has been placed on most of the sites vacated by K that was removed by the degradation treatment. Furthermore, most of this additional $NH_4$ was fixed against extraction by KOH.

The $NH_4$ + K totals, are not necessarily an accurate measure total charge density of the illite, since the amounts of other cations present were not measured. Also, these totals may be low due to the fact that some $NH_4$ may have been lost when both

Table 16. Relationship between the K removed from illite by a NaCl-$NaBPh_4$ degradation and the amount of $NH_4$ adsorbed

| Sample | $NH_4$ and K in me./100 g. | | | |
|---|---|---|---|---|
| | $NH_4$ removed by KOH | Total $NH_4$ | Total K | $NH_4$+K |
| 2B | 25.2 | 27.0 | 90.4 | 117.4 |
| 2C | 30.5 | 71.5 | 46.2 | 117.8 |

samples were heated at 110°C following $NH_4$ saturation. Their similarity, however, would indicate that no great change in charge density occurred during the degradation treatment.

## Resin and Salt Extractions

The early work with resins was carried out with the No. 1 group of illites which did not have the benefit of heat treatment to remove the native nitrogen, nor were they fractionated. Nevertheless, a comparison was made of the ability of Na, H and K-saturated Amberlite IR-120 to extract native and applied $NH_4$ from samples 1A and 1B.

Samples (0.5 g.) of slightly degraded Na-saturated illite 1A and $NH_4$-saturated illite 1B were equilibrated with 10 g. of $NaR_1$, HR and KR for 48 hours in 50 ml. of water. The resin and clay were separated using 150 mesh stainless steel screens, and the $NH_4$ on the resin displaced for quantitative determination by leaching with 350 ml. of 1 N KCl. The amounts of $NH_4$ removed from the two illite by the resins are presented in table 17,

along with the values for total N (by Kjeldahl) and the results of a 24 hour 1 N HCl-HF extraction on sample 1A using the procedure of Bremner and Harada (1959).

Table 17. $NH_4$ removed from $NH_4$-saturated illite samples by resin extractions

| Sample | $NH_4$ removed, me./100 g. | | | | |
|---|---|---|---|---|---|
| | Total N | $NaR_1$ | HR | KR | 1 N HCl-HF |
| 1A | 6.1 | 0.6 | 0.7 | - | 4.6 |
| 1B | 31.4 | 23.8 | 24.6 | 22.7 | - |
| Difference | 25.3 | 23.2 | 23.9 | 22.7 | |
| Unextractable $NH_4$ | | 2.1 | 1.4 | 2.6 | |

The 25.3 me. of $NH_4$ per 100 g. adsorbed by the illite during $NH_4$ saturation was almost all removed by the 3 resins, and KR extracted almost as much as HR. The 6.1 me. of $NH_4$ (native nitrogen per 100 g.) on the other hand, remained largely unaffected by the resins after 48 hours of contact. The HCl-HF mixture does not release nitrogen from organic compounds, therefore at least the 4.6 me. out of this 6.1 me. $NH_4$ per 100 g. it removed must have been present in the natural illite as fixed $NH_4$.

A limited study of the rate of release of $NH_4$ from illite 1B was carried out using 10 g. of HR to 0.5 g. of clay in 50 ml. of $H_2O$, with constant shaking at 25°C for times of contact

varying from 1 hour to 8 days. The results of this study in terms of me. $NH_4$ removed per 100 g. of oven-dry clay are given in table 18.

Table 18. $NH_4$ removed from $NH_4$-saturated illite 1B by HR as a function of time of contact

| | Extraction time | | | | | | |
|---|---|---|---|---|---|---|---|
| | Hours | | | | Days | | |
| | 1 | 3 | 6 | 8 | 2 | 4 | 8 |
| $NH_4$ removed me./100 g. clay | 25.5 | 25.1 | 24.6 | 24.9 | 24.9 | 24.8 | 24.9 |

The exchange of ions that occurred between resin and clay was apparently very rapid since all of the $NH_4$ which was going to be removed had been removed from the clay in 1 hour. Since KR removed 22.7 me. per 100 g. from the same clay (table 17) most of the $NH_4$ adsorbed on this illite during leaching is accessible and thus largely on the edge sites. Therefore, the rate of exchange should have been high since diffusion from interlayer positions was not involved as in the case of vermiculite.

Illite 2C (450°C heated, <20 micron, degraded and $NH_4$-saturated) was also extracted with HR, NaR, and KR. Samples (0.2 g.) of this clay were equilibrated with enough of the various resins to supply 20 me. of the displacing ion, and 20 ml. of water were added to each. Shaking times of 4, 6 and 8 days were

used. Resin and clay were leached together, and the $NH_4$ displaced from the resin using 350 ml. of 1 N KCl per sample. The results are given in table 19.

Table 19. $NH_4$ removed from $NH_4$-saturated, degraded illite 2C by $NaR_1$, HR and KR

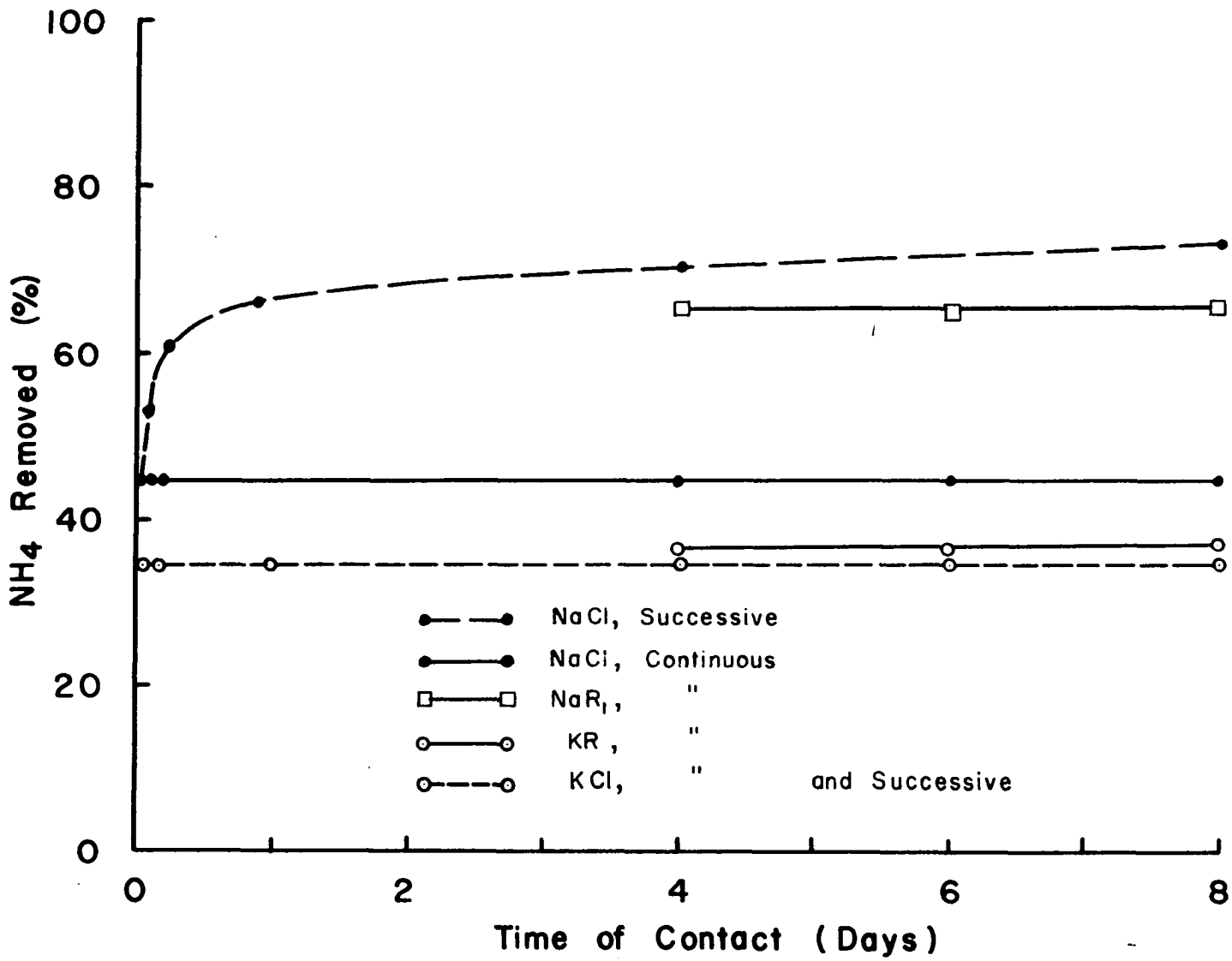
| Time of contact | $NH_4$ removed | | | | | |
|---|---|---|---|---|---|---|
| | $NaR_1$ | | HR | | KR | |
| | me./100g. | % | me./100g. | % | me./100g. | % |
| 4 days | 46.7 | 65.2 | 50.3 | 70.3 | 26.2 | 36.6 |
| 6 days | 46.4 | 64.8 | 50.6 | 70.7 | 26.1 | 36.5 |
| 8 days | 47.0 | 65.6 | 51.7 | 72.2 | 26.6 | 37.2 |

The HR was the only resin to show an increase in the amount of $NH_4$ extracted after 4 days, and even here the increase was slight. The low recovery of $NH_4$ from this degraded illite by $NaR_1$ and HR is strikingly low compared to the 99 percent removed from vermiculite. On the other hand, the percentage of the $NH_4$ in illite 2C removed by KR is about $3\frac{1}{2}$ times as high as the corresponding figure for vermiculite 2B. The greater percentage of exchangeable $NH_4$ in illite as compared to vermiculite can no doubt be attributed largely to the high proportion of edge exchange in finely divided illite. The reason for the relative ineffectiveness of the Na and H-saturated resins in the illite extractions is not immediately apparent. However,

the failure of what were apparently equilibrium extraction values to remove the theoretical amount of $NH_4$ expected on a mass action basis (about 99.3 percent) suggests that the $NH_4$ was very tightly held, and/or that very small amounts of $NH_4$ in solution were effective in blocking further removal of the fixed ions.

A comparison of the Na and K resins with the corresponding chloride salts was made to check further into the effect of accumulations of $NH_4$ in solution upon removal of this cation from the illite. Samples of illite 2B and 2C (0.2 g.) were equilibrated with 20 ml. of 1 N NaCl and 1 N KCl. In order to establish the period of contact between clay and salt required to attain equilibrium, a time study was included as part of the experiment and contact times varying from 1 hour to 8 days were used. Both continuous and successive extractions were made, and in the case of the latter, solutions were changed after 1, 2, 4, 24 and 96 hours of contact. The amounts of $NH_4$ removed from illite 2C, expressed as a percentage of the total of 71.6 me. per 100 g. present, are plotted for the various periods of contact in figure 15. The data obtained with NaR and KR resin equilibrations with illite 2C (table 19) are also plotted for purposes of comparison. The illite 2B data are not shown in figure 15 because the recoveries by both NaCl and KCl were all close together and amounted to over 90 percent of the $NH_4$ present in the undegraded $NH_4$-saturated sample. However, the me. $NH_4$ per 100 g. removed by continuous and successive salt

Figure 15. $NH_4$ removed from $NH_4$-saturated illite 2C by successive and continuous extractions of 0.2 g. of clay with 20 ml. of 1 N NaCl and KCl, and by 20 me. of Na and K as $NaR_1$ and $\overline{K}R$ in 20 ml. of $H_2O$ as influenced by time of contact.


100
80
60
40
20
0
$NH_4$ Removed (%)
0
2
4
6
8
Time of Contact (Days)
NaCl, Successive
NaCl, Continuous
$NaR_1$, "
KR, "
KCl, "
and Successive

extractions of illites 2B and 2C are given in table 20. The total amounts of $NH_4$ present in the two clays were 27.0 and 71.6 me. per 100 g. of oven-dry clay for samples 2B and 2C, respectively.

Table 20. $NH_4$ removed from $NH_4$-saturated illites 2B and 2C by continuous and successive extractions with 1 N NaCl and 1 N KCl using a clay to solution ratio of 1 g. to 100 ml., as a function of time of contact

| Extraction period | me. $NH_4$ removed/100 g. clay | | | |
|---|---|---|---|---|
| | NaCl | | KCl | |
| | Illite 2B | Illite 2C | Illite 2B | Illite 2C |
| | Continuous extraction | | | |
| 1 hour | 24.4 | 32.0 | 23.0 | 24.9 |
| 2 hours | 24.4 | 32.3 | 23.2 | 24.9 |
| 4 hours | 24.3 | 32.0 | 23.6 | 24.9 |
| 4 days | 24.3 | 32.0 | 23.6 | 25.3 |
| 6 days | - | 31.6 | - | 25.3 |
| 8 days | 24.3 | 32.0 | 23.5 | 25.6 |
| | Successive extraction | | | |
| 1 hour | 22.9 | 30.0 | 23.3 | 25.0 |
| 2 hours | 24.3 | 38.5 | 23.3 | 25.3 |
| 4 hours | 24.7 | 43.5 | 23.5 | 25.5 |
| 4 days | 24.8 | 47.3 | | |
| 6 days | 25.0 | 50.3 | | |
| 8 days | 25.3 | 52.6 | | |

The amounts of $NH_4$ removed from both illites 2B and 2C by continuous extractions with NaCl and KCl were much the same for the 8-day as for the 1-hour period of contact. Degraded illite 2C with a total of 71.6 me. of $NH_4$ per 100 g. on the exchange, apparently reached equilibrium as rapidly as undegraded samples 2B and 1B (table 18), that contained only 1/3 as much $NH_4$. These results are a reflection of the fact that $NH_4$ ions on edge exchange sites were principally involved, even in the NaCl extraction of illite 2C. The time of contact therefore, appears to be relatively unimportant where continuous equilibrations are used to remove $NH_4$. However, the amount of $NH_4$ removed from both the degraded and undegraded illites increased with the time of contact in the successive NaCl extractions. It is evident from figure 20 that the curve for successive 1 N NaCl treatments of illite 2C was still rising at an appreciable rate at 8 days.

A blocking effect from replaced $NH_4$ that accumulated in solution is evident in figure 15 from the difference in recovery obtained with successive and continuous extractions with NaCl. The fact that NaR removed less $NH_4$ at 6 and 8 days than the successive NaCl extractions suggests that very small amounts of $NH_4$ in solution are required to block further release of $NH_4$ from the degraded illite.

The accumulation of $NH_4$ in solution had no effect on the release of $NH_4$ from the $NH_4$-saturated illites in the presence of a large excess of K ions, since successive and continuous

extractions with NaCl-KCl solutions gave essentially the same results. The fact that KR removed slightly more $NH_4$ than 1 N KCl (figure 15) could again be due to a grinding effect of the resin on the clay. The very slight upward trend in recovery of $NH_4$ with time by both KR and NaR would also suggest that clay breakdown was occurring.

It is evident from the data in table 15 that very little of the $NH_4$ in the undegraded sample 2B was nonexchangeable. The amounts of $NH_4$ removed by KCl and NaCl were very similar and represented a high proportion of the total of 27.0 me. per 100 g. present. However, the salt solutions did not remove all of the $NH_4$ in the degraded material even where successive extractions were used. The last increment of $NH_4$ is apparently very difficult to remove by treatment with neutral salt solutions, as was also the case with vermiculite.

From the foregoing data on salt and resin extractions of the degraded $NH_4$-saturated illite (2C) it would appear that, although qualitatively the clay behaves like $NH_4$-saturated vermiculite, there are marked quantative differences in the amounts and proportions of the $NH_4$ removed from the two clays. The level of $NH_4$ exchangeable to KCl in the illite was high (32 percent) compared to vermiculite 2B (10 percent). The percentage of the $NH_4$ in illite 2C removed in 8 days by 1 N NaCl was low (45 percent) compared to the 82 percent removed from vermiculite 2B by the same treatment. The amount of $NH_4$ in solution required to block further release of $NH_4$ from a given

amount of clay was therefore greater in the case of the vermiculite. The actual $NH_4$ concentrations at equilibrium (8 days) were 0.064 and 0.134 me. of $NH_4$ per 0.2 g. of clay in 20 ml. of 1 N NaCl for illite 2C and vermiculite 2B, respectively.

## Alkaline Distillations

Distillation in NaOH, in the absence of added K, has been shown to be one of the most effective ways of removing the $NH_4$ in vermiculite, and distillation in KOH an ineffective method. It was demonstrated that the lack of accumulation of $NH_4$ in solution during the NaOH distillation was the principle reason for the ability of this treatment to remove all of the $NH_4$ in the vermiculite in a relatively short time (1 to 2 hours). The large excess of blocking cations and the high pH contributed to the low recovery by KOH. In order to be able to compare the dioctahedral illite with the trioctahedral vermiculite with respect to $NH_4$ recoveries by alkaline distillations, 0.5 g. samples of illite 2B and 2C were boiled continuously in 350 ml. of 1 N NaOH and KOH for periods of 1, 2 and 4 hours. Solution volumes were kept constant by adding $NH_4$-free distilled water drop-wise through separatory funnels. The amounts of $NH_4$ distilled over, expressed as me $NH_4$ per 100 g. of oven-dry clay and as percentages of the total $NH_4$ removed, are given in table 21.

The NaOH did not completely remove the $NH_4$ in the undegraded sample, but it did remove all of the $NH_4$ present in the

Table 21. $NH_4$ removed by boiling $NH_4$-saturated illites 2B and 2C in NaOH or KOH for 1, 2 and 4 hours

| Illite | Distillation time in hrs. | $NH_4$ removed | | | |
|---|---|---|---|---|---|
| | | NaOH | | KOH | |
| | | me./100 g. | % | me./100 g. | % |
| 2B | 1 | 26.4 | 97.8 | 25.0 | 92.6 |
| | 2 | 26.5 | 98.1 | 25.1 | 93.0 |
| | 4 | 26.6 | 98.5 | 25.2 | 93.3 |
| 2C | 1 | 69.5 | 97.1 | 29.2 | 40.8 |
| | 2 | 71.0 | 99.2 | 20.8 | 41.6 |
| | 4 | 71.8 | 100.3 | 30.5 | 42.6 |

degraded sample 2C in a period of 4 hours. The reason for this difference is not clear, unless the small amount of K which may have been displaced into the solution during distillation of the undegraded material blocked the release of the small amount of $NH_4$ present in interlayer positions in sample 2B. The fact that all of the $NH_4$ in illite 2C was replaceable with 1 N NaOH emphasizes the need for complete absence of $NH_4$ in solution before an extractant can be effective.

A comparison of the data in tables 20 and 21 shows that distillations in 1 N KOH were only slightly more effective in removing $NH_4$ than room temperature 1 N KCl extractions with both the degraded and undegraded $NH_4$-saturated illites (table 20). Although the superiority of the KOH could be partly due to $NH_4$ accumulations in solution, since the successive

extractions with KCl were not carried on long enough to say that $NH_4$ had absolutely no effect, the difference between the salt and hydroxide is more likely due to a combination of temperature and pH effects. The level of the exchangeable $NH_4$ determined with KOH or KCl was higher in illite than in vermiculite, as would be expected in view of the smaller particle size of the illite.

The blocking effect of K in the presence of an excess of displacing Na ions was investigated only with the alkaline distillation method of replacing $NH_4$ from illite. Varying amounts of K as dry KCl salt were added to 0.1 g. samples of illite 2C in 800 ml. Kjeldahl flasks. NaOH was added (100 ml. of 1 N) and the contents distilled at constant volume for 1 hour. The amounts of $NH_4$ removed expressed as me. per 100 g. of oven-dry clay, percentage of the total present, and percentage of that fixed against removal by 1 N KOH, are given in table 22. In calculating the percentage of the fixed $NH_4$ removed, the amount removed by 1 N KOH (29.2 me. per 100 g.) was subtracted from the total $NH_4$ (71.6 me. per 100 g.) to arrive at the total fixed $NH_4$ value of 42.4 me. per 100 g. The difference between the amount removed by 1 N NaOH at each level of added K and the 29.2 me. removed by 1 N KOH was then expressed as a percentage of this total fixed $NH_4$ value.

There was a large reduction in the amount of $NH_4$ removed when the first small increment of K was added. The magnitude of the blocking effect from larger additions of K is, however,

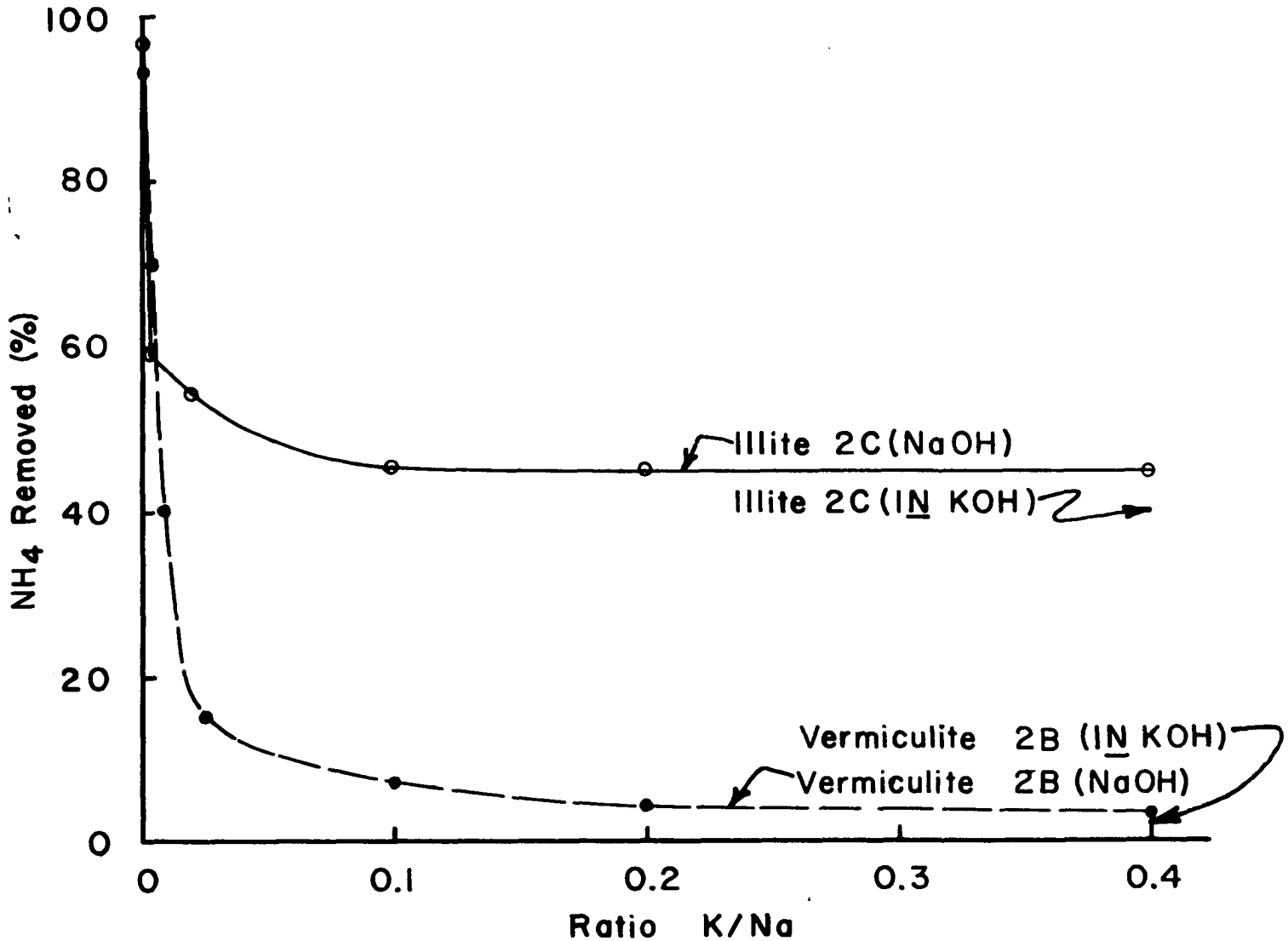
Table 22. The effect of added K upon the amount of $NH_4$ removed from illite 2C by distillation in 1 N NaOH for 1 hour

| K added me./100 ml. | $NH_4$ removed | | |
|---|---|---|---|
| | me./100 g. | % of total | % of fixed |
| 0 | 69.0 | 96.4 | 93.9 |
| 0.5 | 42.1 | 58.8 | 42.5 |
| 2.0 | 38.8 | 54.2 | 34.9 |
| 10.0 | 32.8 | 45.8 | 11.8 |
| 20.0 | 32.6 | 45.5 | 11.1 |
| 40.0 | 32.1 | 44.8 | 9.4 |
| 1 N KOH | 29.2 | 40.8 | 0.0 |

not readily seen from these values for the amount of $NH_4$ removed because so much of the $NH_4$ in illite 2C is not affected by added K.

To better illustrate the relationship between added K and the $NH_4$ removed by NaOH, and to make a comparison between illite 2C and vermiculite, the percentages of the total $NH_4$ removed are plotted in figure 16 against the ratio of K to Na in the extracting solution. The amounts of exchangeable $NH_4$ in the two clays, as reflected in the total removed by 1 N KOH in 1 hour, is also indicated in this figure. In order to bring out difference in behaviour of the fixed $NH_4$ in the two clays, and to minimize particle size effects, the ratio of K to Na in

Figure 16. $NH_4$ removed from illite 2C and vermiculite 2B, as a percentage of the total present in each by boiling 0.1 g. and 1.0 g. respectively in 100 ml. of 1 N NaOH for 1 hour.


100
80
60
40
20
0
NH4 Removed (%)
0
0.1
0.2
0.3
0.4
Ratio K/Na
Illite 2C(NaOH)
Illite 2C(IN KOH)
Vermiculite 2B (IN KOH)
Vermiculite 2B (NaOH)

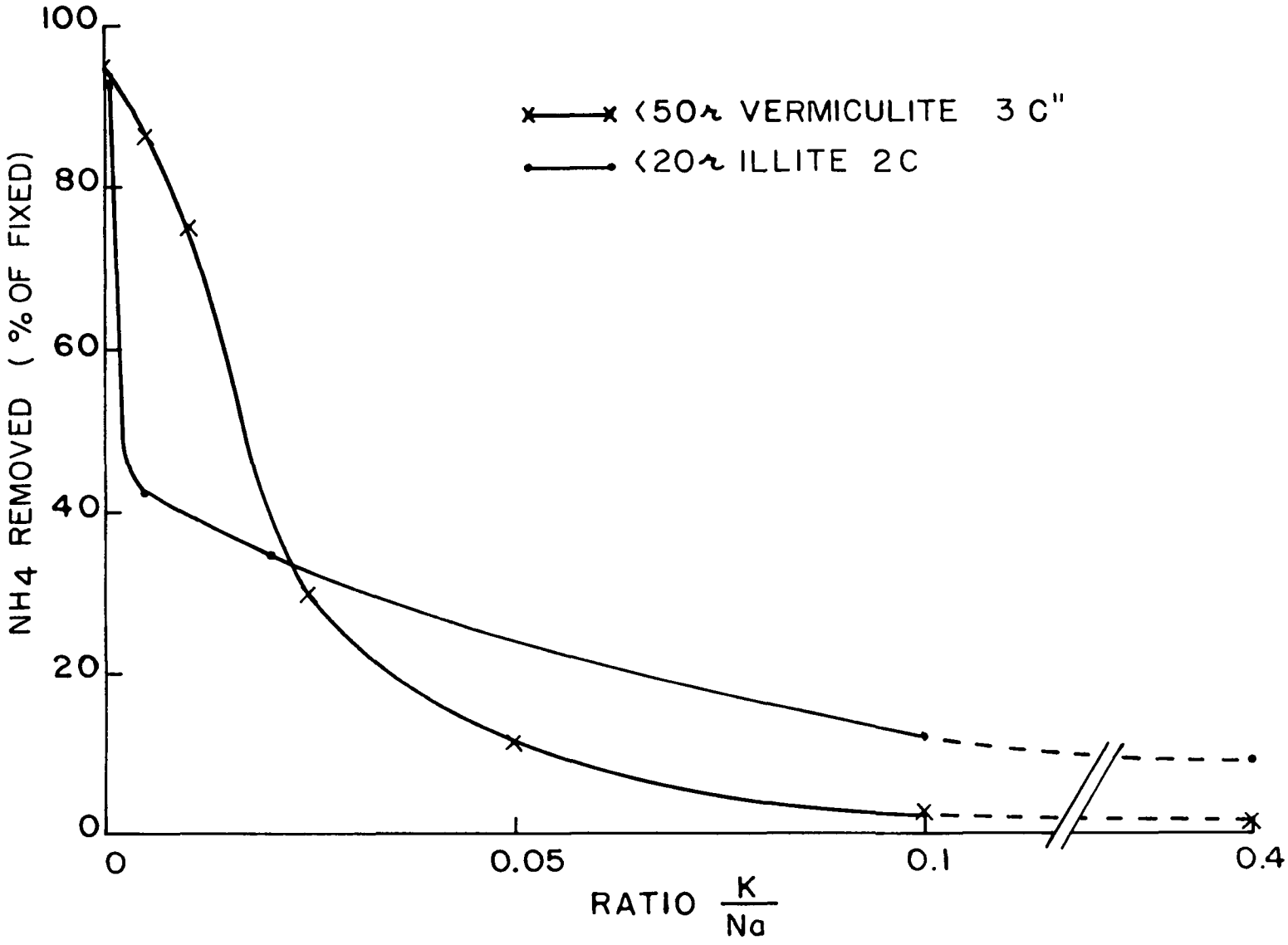
solution has been plotted against the percentage of the fixed $NH_4$ removed from illite 2C ( <20 micron) and vermiculite 3C'' ( <50 micron) in figure 17.

The ratio of K to Na required to reduce the amount of $NH_4$ removed from illite by NaOH to that of 1 N KOH would appear to be higher than the ratio required for complete stoppage of $NH_4$ replacement from vermiculite (figure 16). This point is emphasized in figure 17, which shows a much higher percentage of the fixed $NH_4$ removed by NaOH from the illite at the maximum K to Na ratio of 0.4. In the same figure, the pronounced effect of the first small addition of K in reducing the amount of fixed $NH_4$ which can be removed by the NaOH from illite 2C is striking when compared to the effect of the same K addition on the recovery of fixed $NH_4$ from vermiculite 3C''. It appears, therefore, that some of the fixed $NH_4$ in the illite is readily blocked by small amounts of K, while another fraction is accessible to Na ions even at relatively high K concentrations. Thus, small amounts of both K and $NH_4$ are relatively more effective as blocking agents in reducing the amount of $NH_4$ removed from $NH_4$-saturated illite than they are with $NH_4$-saturated vermiculite.

## Effect of pH

It was observed in the previous section that the greater recovery of $NH_4$ from illite 2C by boiling NaOH and KOH as compared to the corresponding chloride salts could have been due

Figure 17. Percentage of the fixed $NH_4$ removed from < 20 micron $NH_4$-saturated illite 2C and < 50 micron $NH_4$-saturated vermiculite 3C'' by boiling 0.1 and 0.2 g. respectively in 100 ml. of 1 N NaOH for 1 hour.


100
80
60
40
20
0
NH4 REMOVED ( % OF FIXED)
<50r VERMICULITE 3 C"
<20r ILLITE 2C
0
0.05
0.1
0.4
RATIO K/Na

in part to the pH difference. In order to separate out pH effects from those due to differences in temperature, room temperature KOH distillation were compared with 1 N KCl (pH 6.0) extractions. Potassium was used as the replacing cation in order to minimize differences due to accumulations of $NH_4$ in the salt solutions. The KOH distillations at 25°C were accomplished by treating 0.02 and 0.01 g. samples of illites 2B and 2C, respectively, with 4 ml. of 1 N KOH in modified Conway micro-diffusion cells, with intermittent rotation of the contents for a period of 5 days. For the salt extraction 0.2 and 0.5 g. of illites 2C and 2B were equilibrated continuously in 20 and 50 ml. of 1 N KCl, respectively, for 8 days. The results are presented in table 23 as me. of $NH_4$ removed per 100 g. of oven-dry clay. Total $NH_4$ values determined by Kjeldahl analyses and the values for the cumulative amount of $NH_4$ removed by successive extractions with 1 N KCl (3 changes of solution in a total contact period of 4 hours) are also given for purposes of comparison.

The effect of increasing the pH from 6 to 14 had very little influence on the amount of $NH_4$ removed from the $NH_4$-saturated illite. The slightly higher results with the KOH as previously mentioned, could be explained by postulating a small blocking effect due to $NH_4$ in the KCl solution. The successive KCl extraction results do not support this conclusion but these extractions were carried on for only 4 hours. If several more changes of solution and a longer total contact time had been used it is possible that the successive KCl extractions might

Table 23. $NH_4$ removed from illites 2B and 2C by 1 N KCl and 1 N KOH solutions at 25°C

| Sample | $NH_4$ removed, me./100 g. | | | |
|---|---|---|---|---|
| | Total | KOH | KCl (continuous) | KCl (successive) |
| 2B | 27.0 | 24.2 | 23.5 | 23.5 |
| 2C | 71.6 | 26.8 | 25.6 | 25.5 |

have also removed slightly more $NH_4$ than the continuous KCl extractions. In any event the effect of pH changes in the alkaline range appears to be minor.

To investigate the effect of pH changes in the acid range, solutions 1 N in $Na_3C_6H_5O_7$ were adjusted to 2 pH levels (3.9 and 6.9) with citric acid. Samples of illites 2B and 2C (0.5 and 0.2 g., respectively) were equilibrated with these solutions for periods of 2 and 14 hours. A clay to solution ratio of 1 g. to 100 ml. was used for both clays. The amount of $NH_4$ removed from the illites is given in table 24 as me. $NH_4$ removed per 100 g. of oven-dry clay.

The difference of 3 pH units had very little influence on the amount of $NH_4$ removed from either illite sample, although recoveries were slightly higher at the lower pH. Vermiculite, over the same range of acidity, showed a difference in recovery of $NH_4$ by 1 N NaCl of about 15 me. per 100 g. in favor of the acidified solution.

The differences in the amounts of $NH_4$ removed by HR and NaR

Table 24. $NH_4$ removed from $NH_4$-saturated illites 2B and 2C by 1 N $Na_3C_6H_5O_7$ at 2 pH levels

| Contact time hours | $NH_4$ removed, me./100 g. | | | |
|---|---|---|---|---|
| | Illite 2B | | Illite 2C | |
| | pH 3.9 | pH 6.9 | pH 3.9 | pH 6.9 |
| 2 | 25.1 | 24.0 | 32.6 | 31.2 |
| 14 | 25.1 | 24.3 | 32.9 | 31.6 |

already shown in table 19 were likewise small. Therefore in both the resin and soluble salt extractions pH was not an important factor with illite. The differences between the amounts of $NH_4$ removed by NaOH and NaCl, and by KOH as compared to KCl, were apparently influenced to a minor degree by the pH differences of the extractants.

Temperature of the Extracting Solution

The effect of the temperature of the extractant on the amount of $NH_4$ removed from illite was determined over the range of temperatures from 4°C to 100°C.

Boiling and room temperature distillations with 1 N NaOH and 1 N KOH solutions were carried out with illites 2B and 2C. For the boiling distillations, 0.5 and 0.2 g. of illites 2B and 2C, respectively, were boiled for 4 hours in 350 ml. of both 1 N KOH and 1 N NaOH. The room temperature extractions with these solutions required 0.02 g. of clay in 4 ml. of base in modified Conway micro-diffusion cells. Equilibration was

for 8 days at 25°C with occasional swirling of the dishes to mix the clay and solution. The amounts of $NH_4$ collected in boric acid at both temperatures are given in table 25 as me. $NH_4$ removed per 100 g. of oven-dry clay.

Table 25. $NH_4$ removed from $NH_4$-saturated illites 2B and 2C by distilling in NaOH and KOH at 25° and 100°C

| Sample | $NH_4$ removed, me./100 g. | | | | |
|---|---|---|---|---|---|
| | By Kjeldahl | KOH | | NaOH | |
| | | 25°C | Boiling | 25°C | Boiling |
| 2B | 27.0 | 24.2 | 25.2 | 25.4 | 26.6 |
| 2C | 71.6 | 26.8 | 30.5 | 64.0 | 71.8 |

The boiling distillations gave consistently higher results, although the differences were appreciable only in the case of the degraded illite 2C with the high $NH_4$ content. Since this occurred with both KOH and NaOH, it would suggest that some of the interlayer $NH_4$ was being released because the bases were actually dissolving or destroying part of the clay. However, there is also the possibility that the slower conversion of $NH_4$ to $NH_3$ at the lower temperature permits enough $NH_4$ to remain in the solution phase long enough to interfere with the removal of the $NH_4$ in the illite.

Extractions of illite 2C at temperature of 4°, 25°, 50°, 75° and 100°C were made with NaCl and for all but the 4°C temperature with KCl. Samples (0.2 g.) of the degraded illite

were equilibrated in 20 ml. of 1 N NaCl or KCl in 50 ml. flasks and were shaken continuously in constant temperature rooms for the two low temperatures. For the higher temperature, samples of the same size were weighed into 100 ml. polypropylene centrifuge tubes, and the tubes were fitted with reflux condensers during equilibration in a water bath. The results in terms of me. $NH_4$ removed per 100 g. of oven-dry clay, and the various extraction times used, are given in table 26.

Table 26. Effect of extraction temperature on the amount of $NH_4$ removed from $NH_4$-saturated illite 2C by 1 N NaCl and 1 N KCl

| Temp., °C | Contact time days | $NH_4$ removed, me./100 g. | | | |
|---|---|---|---|---|---|
| | | NaCl | | KCl | |
| | | me. | % | me. | % |
| 4 | 12, 18 | 31.6 | 44.1 | - | - |
| 25 | 8 | 32.0 | 44.7 | 25.3 | 35.3 |
| 50 | 6 | 32.2 | 45.0 | 25.2 | 35.2 |
| 75 | 6 | 32.8 | 45.8 | 25.2 | 35.2 |
| 100 | 4 | 33.5 | 46.8 | 25.2 | 35.2 |

The data in table 26 show that the effect of temperature on the amount of $NH_4$ removed by NaCl was very small. This is a contrast to the high temperature effect observed with vermiculite. The KCl extraction results showed no temperature influence whatsoever.

The natural illite (Goose Lake Grundite) was shown to contain an appreciable amount of native nitrogen, partly organic and partly fixed $NH_4$. This nitrogen was completely removed by heating the clay at 450°C for 24 hours. The natural material likewise fixed small amounts of $NH_4$ whether heated or unheated. Removal of K by degrading the illite with NaCl-$NaBPh_4$ made it possible to prepare material with total $NH_4$ contents as high as for some natural vermiculites and bentonites. Extractions of degraded and undegraded heated illites showed that small amounts of $NH_4$ or K in solution were able to block release of $NH_4$ to salts, resins and NaOH. Attainment of equilibrium levels of extraction was much more rapid with the $< 20$ micron illite than was the case with coarser vermiculite. The $NH_4$ removal from both degraded and undegraded illites was relatively unaffected by temperature or by changes in pH between 4 and 14. The higher recovery of $NH_4$ by NaOH as compared to neutral NaCl appeared to be largely the result of the absence of an accumulation of $NH_4$ in the NaOH solution. The relatively high effectiveness (compared to vermiculite) of KOH in removing $NH_4$ from illite was attributed to the high proportion of edge sites in the finely divided illite. The fact that the resins and salts did not remove nearly as high a percentage of the total $NH_4$ from the degraded illite as they did from vermiculite appeared to be related to the relatively high blocking effects of very small amounts of $NH_4$ upon the removal of the $NH_4$ in the illite. The degraded $NH_4$-saturated illite proved to be highly sensitive to

small amounts of K in solution when NaOH distillations were used to replace the $NH_4$.

## REMOVAL OF AMMONIUM FROM BENTONITE

Although soils containing colloidal material identified as montmorillonite have been shown to fix $NH_4$, it is difficult to prepare natural bentonites that will retain $NH_4$ against KCl or KOH in appreciable quantities. Allison and Roller (1955) found very small amounts (1 me. per 100 g.) were fixed against KOH distillations when 5 bentonites were $NH_4$-saturated and dried at 110°C in the presence of excess $NH_4Cl$. They also found, however, that fixation values as high as 15 me. per 100 g. occurred in bentonite that was leached with 1 N $Na_2CO_3$ prior to $NH_4$ saturation. Hanway, Scott and Stanford (1957) reported only 2 me. of $NH_4$ fixed after drying Wyoming bentonite at 110°C in the $NH_4$-saturated state, but appreciable amounts were fixed in the same clay by heating in a muffle at 350°C for 24 hours following $NH_4$ saturation. The same authors found the heated $NH_4$-saturated bentonite to behave similarly to vermiculite with respect to the blocking effects of $NH_4$ and K added to the clay prior to extraction with NaCl. Welch (1958) showed that the $NH_4$ in bentonite prepared in this manner was only partially available to nitrifying bacteria.

Since little information was available on the mechanism of $NH_4$ fixation in bentonite by heating, it was decided to compare a variety of extraction techniques on $NH_4$-saturated clays dried at both 110°C and 350°C. The number 1 and 2 groups of bentonite samples described under "Material and Methods" were therefore

prepared for studies on the replaceability of ammonium. Briefly, group 1 samples were obtained by heating at the two temperatures following $NH_4$ saturation of the natural bentonite with no pre-treatment. The material for the group 2 samples was first heated at 450°C for 24 hours in the natural (Na-saturated) state to remove the 1.1 me. $NH_4$ (native nitrogen) per 100 g. present, $NH_4$ saturated and fractionated to obtain < 2 micron material. Again, heating temperatures of 110°C and 350°C were used on different portions of this material following $NH_4$ saturation and alcohol washing. Thus, samples 1B and 2B were dried at 110°C, samples 1C, 1D and 2C at 350°C. Samples 1C and 1D differed only in that they were prepared at different times and heated in different muffle furnaces.

## Resin, Salt and Alkali Extractions

The total N in the various bentonite samples was determined by Kjeldahl analysis. Then, following the same procedure as used in the illite and vermiculite extractions, the bentonite samples were treated with various salts, alkalis and cation exchange resins. The results obtained are summarized in table 27. Ratios of clay to extractant and the extraction period are also shown in the table for each extraction, and all solutions were used at a concentration of 1 N. Ratios of clay to extractant refer to g. of clay to g. of resin or to ml. of solution, whichever applies. The extractions were all carried out at 25°C, with the exception of the boiling NaOH and KOH distillations.

Table 27. $NH_4$ removed from $NH_4$-saturated bentonites heated to 110°C or 350°C by salts, resins NaOH and KOH

| Treatment | Time (days) | Clay extr. | $NH_4$ removed, me./100 g. | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1B | 1C | 1D | 2B | 2C |
| Kjeldahl | | | 76.8 | 20.5 | 50.4 | 82.6 | 41.5 |
| $NaR_o$ | 2 | 1/10 | | 2.1 | | | |
| $NaR_o$ | 2 | 1/20 | 73.5 | 2.4 | 36.3 | | |
| NaR | 2 | 1/10 | | 3.1 | | | 24.2 |
| NaR | 8 | 1/25 | | | | 80.6 | |
| HR | 2 | 1/10 | | 2.6 | | | |
| HR | 2 | 1/20 | | 2.1 | 35.1 | | |
| HR | 8 | 1/20 | | | 36.7 | | |
| KR | 2 | 1/10 | | 0.84 | | | |
| KR | 2 | 1/20 | | | 9.0 | | |
| KCl | - | 0.2/20 | | | | 74.6 | 1.7 |
| NaCl | 4 | 0.3/20 | | 2.2 | 33.0 | | |
| NaCl | 4 | 0.2/20 | | | | 79.9 | 20.2 |
| NaOH boiling | 1/24 | 0.5/350 | | 18.3 | 43.1 | 82.6 | 34.9 |
| KOH boiling | 1/24 | 0.5/350 | 74.6 | 7.4 | 27.1 | 80.9 | 18.4 |
| NaOH | 5 | 0.02/4 | | | | 76.7 | 33.2 |
| KOH | 5 | 0.02/4 | | | | 73.8 | 18.7 |

There was very little $NH_4$ in the bentonites dried at 110°C (1B, 2B) which was not removed by boiling for 1 hour in 1 N KOH. The 2.2 and 1.7 me. $NH_4$ per 100 g. fixed in samples 1B and 2B, respectively, are much lower, especially on a percentage basis, than the 13.1, 23.3 and 23.1 me. of $NH_4$ per 100 g. which were not removed by KOH from the 350°C heated samples 1C, 1D and 2C, respectively. The heat treatment at 350°C therefore increased the amounts of fixed $NH_4$ in the bentonites. This increased fixation occurred in spite of the loss of 1/4 to 2/3 of the total $NH_4$ present.

Distillation of bentonite 2B (dried at 110°C) in 1 N NaOH for 1 hour removed all of the $NH_4$ present. The amount of $NH_4$ removed from the samples heated at the higher temperature (350°C), although greater by NaOH distillation than by any other extraction, fell about 10 to 15 percent short of removing the total shown to be present by Kjeldahl analysis.

There was little difference in the amounts of $NH_4$ removed by NaCl and $NaR_1$ from the 110°C dried material (2B) or from the 350°C heated bentonites 1C, 1D and 2C. None of the resins ($NaR_0$, $NaR_1$ or HR) came as close to theoretical effectiveness as $NaR_1$ did in the case of vermiculite. The high pH of the NaOH appears to be the important factor in determining the effectiveness of this extractant on the oven-dried (110°C) materials, since KOH removed almost as much $NH_4$ as NaOH from sample 2B, and more than the resins or NaCl. There is of course the possibility that increasing the temperature of the

extracting solution had a positive influence on the amounts of $NH_4$ removed from bentonite, in contrast to the lack of effect in the case of illite and the negative effect observed with vermiculite. The lower recoveries by the NaOH and KOH room temperature as compared to the boiling distillations (sample 2B) would seem to point to the existence of a positive influence of higher temperatures on the amount of $NH_4$ removed from bentonite.

Temperature of the Extracting Solutions

In the search for methods of recovering the $NH_4$ present in sample 1C it became apparent that increasing the temperature did have a marked positive effect on the amount of $NH_4$ removed by certain salts and resins. To study the influence of temperature further, and to determine if the anion had an influence on the recovery of $NH_4$, samples of bentonite 1C (0.5 g.) were equilibrated for periods of 2 and 8 days with 20 me. of Na as NaCl, $NaR_1$ and $Na_3C_6H_5O_7$ in 20 ml. of $H_2O$. The citrate solutions were used at 3 pH levels (7.3, 6.5 and 3.5). The samples were shaken continuously at 25°C or were boiled vigorously on a hot plate in flasks fitted with reflux condensers. The amounts of $NH_4$ extracted by the various solutions at one or both of the temperatures are given as me. $NH_4$ removed per 100 g. of oven-dry clay in table 28. Bentonite 1C contained a total of 20.5 me. $NH_4$ per 100 g.

The data in table 28 suggest that the increased recovery

Table 28. $NH_4$ removed from $NH_4$-saturated bentonite 1C as affected by the temperature of the extractant

| Extractant | $NH_4$ removed, me./100 g. | | | |
|---|---|---|---|---|
| | 2 days | | 8 days | |
| | 25°C | 100°C | 25°C | 100°C |
| NaCl | 2.2 | 7.1 | | 11.1 |
| $NaR_1$ | 2.6 | 4.7 | 3.1 | 13.4 |
| $Na_3C_6H_7O$ pH 7.3 | 4.5 | 14.5 | | |
| $Na_3C_6H_5O_7$ pH 6.5 | | 15.6 | | |
| $Na_3C_6H_5O_7$ pH 3.5 | | 10.3 | | |

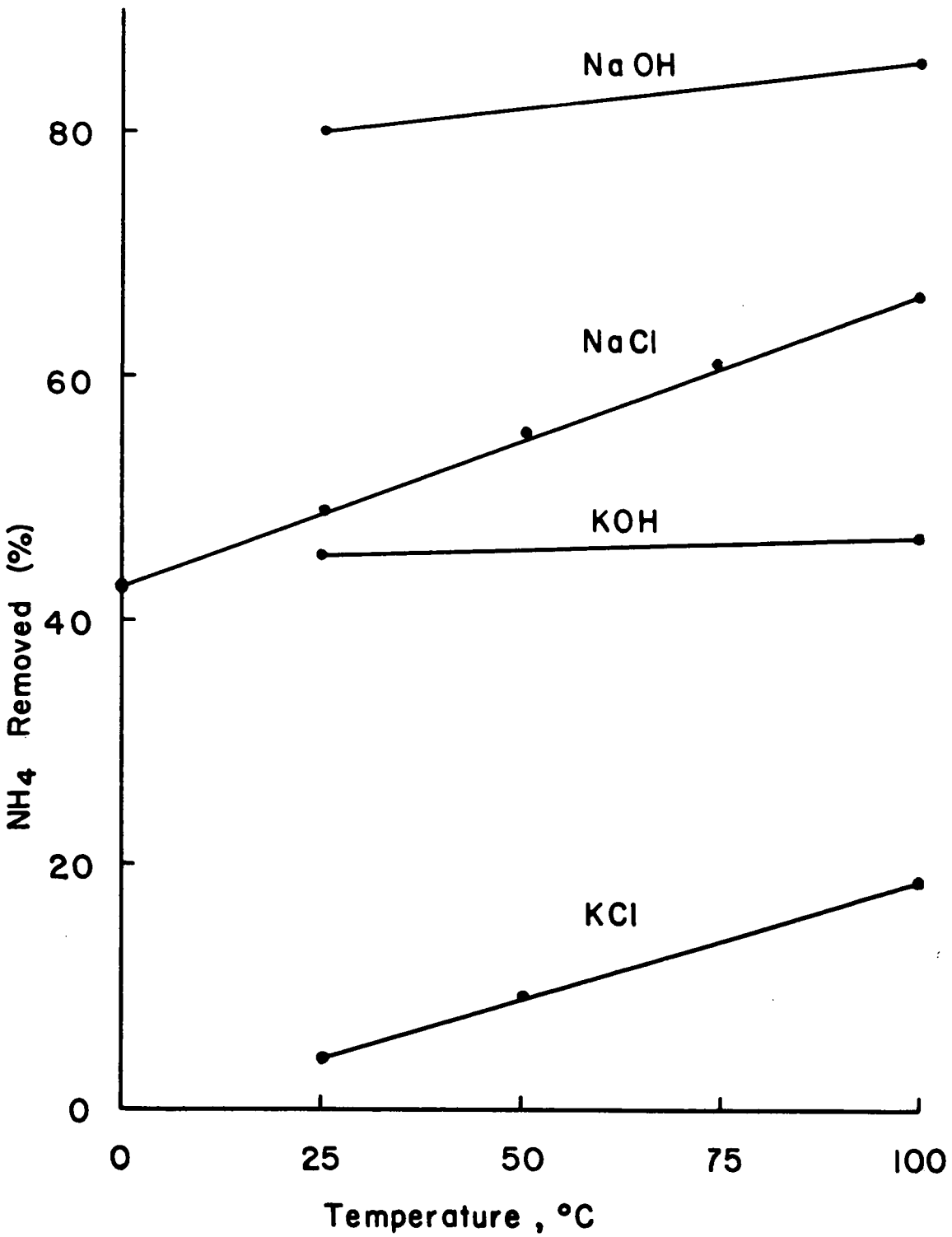
of $NH_4$ at the higher temperatures had more than one cause. The higher amount removed by NaCl in 2 days at 100°C as compared to 25°C suggests that the solubility of a slightly soluble compound may be involved. Furthermore, the $Na_3C_6H_5O_7$ removed more $NH_4$ in 2 days at 25°C than either the NaCl or $NaR_1$ and the citrate salt at pH 6.5 removed more $NH_4$ in 2 days at 100°C than the resin and salt extracted from the bentonite in 8 days at the boiling temperature. The anion, therefore, had an effect. The citrate may have removed or complexed some interfering substance or ion like Al.

Further investigations were made into the removal of $NH_4$ from bentonite 2C (heated at 350°C in the $NH_4$-saturated state) by neutral NaCl and KCl solutions over a range of temperatures

from 4° to 100°C. Samples of this bentonite (0.5 g.) were shaken continually in constant temperature rooms at 4° and 25°C with 20 ml. of 1 N NaCl and 1 N KCl. The same amounts of clay and solution were added to polypropylene centrifuge tubes fitted with reflux condensers, and a water bath was used to maintain the temperature at 50°, 75° and 100°C. Boiling distillations in 1 N KOH and 1 N NaOH, using a ratio of clay to solution of 0.5 g. to 350 ml., were also carried out for a period of 4 hours. The volume of solution in the distilling flasks was maintained at a constant level by addition of distilled water through separatory funnels. Room temperature distillations in modified Conway micro-diffusion cells were conducted over a 5 day period using 0.02 g. of bentonite 2C and 4 ml. of 1 N NaOH and 1 N KOH. The results of these determinations are plotted in figure 18 as the percentage of the $NH_4$ removed. Bentonite 2C contained 41.5 me. of $NH_4$ per 100 g. of oven-dry clay as determined by an extended Kjeldahl analysis.

There was little difference between the amount of $NH_4$ removed by the boiling and room temperature distillations in NaOH, and even less difference between the results at the two temperatures in the case of KOH. Solubility was therefore not an important factor at a high pH. The fact that the KOH removed a much higher proportion of the $NH_4$ in the bentonite than the KCl solution may have been due to the need for neutralizing the acidity of the clay in order to permit removal of a high proportion of the total $NH_4$ present.

Figure 18. $NH_4$ removed from $NH_4$-saturated bentonite 2C by NaCl, KCl, NaOH and KOH as influenced by extraction temperature.


NaOH
NaCl
KOH
KCl
80
60
40
20
0
$NH_4$ Removed (%)
0
25
50
75
100
Temperature , °C

The difference between the amounts of $NH_4$ removed from bentonite 2C by NaCl and KCl was approximately the same as the difference between the amounts extracted by NaOH and KOH (18.5 and 14.5 me. respectively). These differences would appear to be a reflection of the amount of interlayer $NH_4$ in this clay actually affected by K blocking.

The increase in the amount of $NH_4$ removed from the bentonite as the temperature increased is directly opposite to the effect observed with the vermiculite. However, the true relationship between temperature and the replaceability of fixed $NH_4$ in the 350°C heated bentonite may be obscured by side effects having to do with solubility of N-containing compounds outside the clay lattice.

## Miscellaneous Treatments

A boiling distillation in NaOH removed the highest percentage of the $NH_4$ in bentonite 2C during the temperature study, and amounted to only slightly over 80 percent of the total present. A study was therefore made of the effect of time on the amount of $NH_4$ removed from both 110°C dried (2B, 3B) and 350°C heated (2C, 3C) bentonite by boiling NaOH and KOH. Also, in the case of bentonite 2C, 3 successive extractions with NaOH were tried to determine if an accumulation of soluble material could be involved in the relatively low recovery. The continuous 1 N NaOH and 1 N KOH distillations were carried out for 1, 2 and 4 hour periods using 0.2 and 0.5 g. of bentonite 2B

and 2C, respectively, in 350 ml. of base. The volume of solution was maintained close to 350 ml. by the addition of $NH_4$-free distilled water at the same rate as distillate was collected in the receiving flask. The successive distillation of sample 2C in NaOH was accomplished in the same manner, excepting that the clay was filtered and fresh NaOH solution was added after 1 and 2 hours. The amount of $NH_4$ in the combined distillate from the 1 and 2 hour extractions, and again after an additional 2 hours of boiling was determined. The amounts of $NH_4$ removed, expressed as me. per 100 g. of oven-dry clay, are given in table 29. The total $NH_4$ contents of the various clays, as determined by Kjeldahl analysis, are also tabulated.

The samples dried at 110°C (2B, 3B) had all of their $NH_4$ removed in 1 hour by NaOH, and essentially all in 4 hours by KOH. The samples heated at 350°C, however, did not release more than 50 percent of their $NH_4$ to KOH, and both continuous and successive extractions of samples 2C with NaOH removed less than 36 me. out of the 41.5 present even after 4 hours of contact. The increase in the amount of $NH_4$ removed with increasing time of contact was very slight, amounting to only about 1 me. per 100 g. for both KOH and NaOH for the last 3 hours of boiling. The fact that successive extractions in NaOH did not increase the recovery of $NH_4$ from sample 2C indicates that there was no interference from substances or ions in solution.

Various 1 N salt solutions were compared to find out whether the presence of certain anions known to be capable of

Table 29. Effect of distillation time on the amount of $NH_4$ removed from $NH_4$-saturated bentonites 2B, 2C, 3B and 3C

| Extraction | Time in hours | $NH_4$ removed, me./100 g. | | | | |
|---|---|---|---|---|---|---|
| | | 3B | 3C (continuous) | 2B | 2C | 2C (successive) |
| Kjeldahl anal. | - | 79.7 | 35.9 | 82.6 | 41.5 | 41.5 |
| NaOH distill. | 1 | | | 82.6 | 34.9 | - |
| NaOH distill. | 2 | | | - | 35.0 | 34.7 |
| NaOH distill. | 4 | | | - | 35.9 | 35.6 |
| KOH distill. | 1 | 78.1 | 17.2 | 80.9 | 18.4 | |
| KOH distill. | 2 | 78.6 | 17.8 | 81.4 | 18.8 | |
| KOH distill. | 4 | 79.2 | 18.3 | 82.2 | 19.2 | |

complexing polyvalent cations such as $Al^{3+}$ would result in any increase in the amount of $NH_4$ removed from sample 2C. Portions (0.5 g.) of this clay were equilibrated for 8 days at 25°C in 20 ml. of 1 N NaCl and 1 N NaF at 2 pH levels (8.4 and 6.0) and the $NH_4$ determined in the filtrates. Since higher temperatures had previously been shown (table 28) to increase the recovery of $NH_4$ from bentonite 1C by salts and resins, 0.5 g. samples of bentonite 2C were also refluxed for 24 hours in NaCl, NaF, $Na_3C_6H_5O_7$, $NaH_2PO_4$, $Na_4P_2O_7$ and NaCl-$Na_2C_2O_4$ solutions all 1 N in Na, and the $NH_4$ released was distilled from the solution in the presence of the clay by adding KOH and boiling for 2 and 4 hours. The results of these experiments are given in table 30

as me. $NH_4$ removed per 100 g. of oven-dry clay.

Table 30. $NH_4$ removed from 350°C heated $NH_4$-saturated bentonite 2C by 1 N Na salts at 25°C and by boiling

| Extracting solution | $NH_4$ removed, me./100 g. | | |
|---|---|---|---|
| | 25°C | Boiled 24 hours | |
| | Filtrate distilled | Distilled 2 hours | Distilled 4 hours |
| NaCl (pH 6.0) | 20.6 | 31.3 | 31.8 |
| NaF (pH 8.4) | 29.7 | variable, low | |
| NaF (pH 6.0) | 30.3 | | |
| $Na_3C_6H_5O_7$ (pH 5.9) | | 32.0 | 32.2 |
| $NaH_2PO_4$ | | 32.0 | |
| $Na_4P_2O_7$ | | variable, low | |
| NaCl-$Na_2C_2O_4$ | | variable, low | |

There was little difference between the $NH_4$ removed by the 3 salts at the high temperature, again suggesting a solubility relationship rather than the need for complexing an interfering ion. The instability of $NH_4$ in solutions of NaF, $Na_4P_2O_7$ and $Na_2C_2O_4$ was evident, although the high pH of the NaF no doubt contributed to the loss of $NH_3$. The recoveries in all cases were below the 36 me. of $NH_4$ per 100 g. removed by 1 N NaOH, again pointing out the need for a high pH to obtain maximum displacement of $NH_4$ from the 350°C heated $NH_4$-saturated bentonite.

In this experiment the replaced $NH_4$ in the equilibrated

bentonite-extracting salt mixture was determined by adding KOH to the mixture. Some of the $NH_4$ removed, therefore, could have been due to the KOH distillation and not to the previous salt extraction. Therefore, a comparison was made between direct 1 hour boiling distillations that were started immediately after the addition of 20 ml. of 1 N sodium citrate buffer (pH 5.9) or after a 24 hours reflux period in the same sodium citrate solution. The amounts of $NH_4$ removed were the same in all cases (about 32 me. $NH_4$ per 100 g. of clay). Thus the sodium citrate extraction did not remove any $NH_4$ that was not removed by the sodium borate distillation.

The results obtained with the various extraction procedures and 350°C heated bentonites, indicate that only part of the total nitrogen was present as interlayer $NH_4$ which was not available to displacement by K salts. Relatively insoluble nitrogen containing compounds, removed in increasing amounts by raising the temperature and the pH, were also present. A third and more resistant fraction of the total nitrogen, present as $NH_4$ or compounds converted to $NH_4$ by digestion in sulfuric acid, was extractable only by Kjeldahl digestion. In carrying out Kjeldahl analysis on the heated bentonite samples, it was noted that breakdown of the very dark colored clay did not really begin until after the catalyst was added. Since, as pointed out under "Methods and Materials", the acid-catalyst mixture boiled at about 350°C, it would appear that these resistant nitrogen-containing compounds formed by heating $NH_4$-saturated bentonite

to 350°C require a high temperature acid extraction before decomposing. A prolonged digestion at the high temperature was also required for complete recovery of the nitrogen present.

## Effect of Various Treatments on the Adsorption and Fixation of $NH_4$ by Bentonite

The failure to achieve any degree of $NH_4$ fixation by Wyoming bentonite without resorting to a drastic heat treatment led to a study of the effect of different methods of preparing $NH_4$-saturated bentonites. According to Sawhney (1958), interlayer Al can reduce the exchange capacities of montmorillonite clays, and can restrict the lattice expansion and thereby cause montmorillonite to be mistaken for vermiculite in acid soils. Dion (1944) showed that iron oxides may interfere with ion exchange by a coating or clogging action. Grim (1953) states that organic matter and sulfur compounds can also interfere with the exchange of cations and reduce the exchange capacities of clays, but these are probably not factors in the present study with bentonites heated at 450°C to remove organic nitrogen. It is also conceivable that the K in the bentonite sample is already occupying most of the interlayer sites capable of holding fixable cations in nonexchangeable form. Thus, there are several factors that could be responsible for the lack of $NH_4$ fixation in bentonite. The objective of this study, therefore, was to explore the possibility of using various treatments to enhance the adsorption and fixation of $NH_4$ by bentonite.

To investigate the effect which naturally occurring K

might have on $NH_4$ adsorption and fixation in bentonite, portions of the 450°C heated < 2 micron bentonite were treated with NaCl-$NaBPh_4$ to remove part of the potassium. These degraded samples, designated as 3B and 3C and described in table 3, were then compared to samples 2B and 2C as to K content. All of the samples contained 0.48 me. of K per 100 g. Therefore, the K in the montmorillonite material used is not easily removed by cation exchange methods. This K may be present between the layers of a mica component or it may be present in finely divided feldspar. In either event, these sites are not normally involved in the adsorption and fixation of $NH_4$ by bentonite and they are not easily activated for this purpose.

Attention was therefore directed toward the effect of Al and Fe in the bentonite, either as oxides or cations. The same $NH_4$-free, 450°C heated, Ca-saturated < 2 micron Wyoming bentonite (sample 2A, table 3) that was used in preparing samples 2B and 2C was subjected to various treatments and $NH_4$-saturated. The nature of these treatments and their effect on total (Kjeldahl analysis) and exchangeable (KOH distillation) $NH_4$ in the material are given in table 31. In the KOH distillations 0.25 g. samples of bentonite were distilled in 350 ml. of 1 N KOH for 1 hour. The values obtained with samples 2B, 2C, 3B and 3C are also included for comparison.

It is evident from table 31 that one of the major factors determining the amount of $NH_4$ in $NH_4$-saturated bentonite samples is the drying temperature. Increasing the drying temperature

Table 31. Effect of various treatments on the total and exchangeable $NH_4$ adsorbed by 450°C heated, <2 micron Ca-saturated Wyoming bentonite

| Bentonite sample | Treatment | $NH_4$ determination, me./100g. Total (Kjeldahl) | Exchangeable (KOH) |
|---|---|---|---|
| 2B | $NH_4$-saturated dried 110°C | 82.6 | 80.9 |
| 2C | $NH_4$-saturated dried 350°C | 41.5 | 18.4 |
| 3B | Degraded, $NH_4$-saturated dried 110°C | 79.7 | 78.1 |
| 3C | Degraded, $NH_4$-saturated dried 350°C | 35.9 | 17.2 |
| $T_1$ | 30 hrs. in boiling 1 N $Na_3C_6H_5O_7$ (pH 7.3) $NH_4$-saturated dried 110°C | 83.2 | - |
| $T_2$ | 15 min. in 80°C. 0.3 M $Na_3C_6H_5O_7$-$NaHCO_3$ buffer, + $Na_2S_2O_3$, 24 hr. NaCl-$NaBPh_4$ degradation, $NH_4$-saturated dried 110°C | 89.2 | - |
| $T_3$ | 24 hrs. in boiling 1 N $(NH_4)$ $C_6H_6O_7$ (pH 4.7) $NH_4$-saturated dried 110°C | 85.1 | - |
| $T_{4a}$ | 15 min. in 80°C 0.3 M $Na_3C_6H_5O_7$-$NaHCO_3$ buffer + $Na_2S_2O_3$, 24 hr. NaCl-$NaBPh_4$ degradation, $NH_4$-saturated dried 110°C | 78.5 | - |
| $T_{4b}$ | Same as $T_{4a}$ but dried 350°C | 30.3 | - |
| $T_{5a}$ | 2-15 min. treatments in 0.3 M $Na_3C_6H_5O_7$-$NaHCO_3$ buffer + $Na_2S_2O_3$, 7 hrs. in 95°C 1 N $Na_3C_6H_5O_7$, $NH_4$-saturated dried 25°C | 102.1 | 94.9 |
| $T_{5b}$ | Same as $T_{5a}$ but dried 110°C | 88.0 | 80.2 |
| $T_{5c}$ | Same as $T_{5a}$ but dried 350°C | 60.1 | 35.2 |

from 25° to 110°C resulted in an appreciable loss of $NH_4$ but no change in the amount of $NH_4$ fixed. When the $NH_4$-saturated samples were heated at 350°C there was also a large loss of $NH_4$. At this temperature, however, much of the $NH_4$ was fixed. These results therefore confirm previous observations that drying at an elevated temperature is required for appreciable $NH_4$ fixation in bentonite. A comparison of 2C, 3C, $T_{4b}$ and $T_{5c}$, however, shows that bentonite samples with quite different amounts of total and fixed $NH_4$ can be obtained by the same 350°C heat treatment. It is also possible that the fixed $NH_4$ in these samples may vary as to ease of replacement.

The treatment with NaCl-$NaBPh_4$ did not increase the amount of $NH_4$ adsorbed or fixed. This was to be expected since it was shown above that this degradation treatment did not remove K from the bentonite.

The boiling citrate and the dithionite treatments should have removed Fe and Al oxide coatings from the clay particles. In fact Sawhney (1958) showed that boiling 14Å soil clays in sodium citrate in this manner resulted in an expansion of the mineral lattice to 17Å. Therefore it is not surprising that this treatment increased both the total and fixed $NH_4$ in the bentonite. The increase in $NH_4$ adsorption was only a few me. per 100 g., but most of the additional $NH_4$ adsorbed was fixed. Even the air dried (25°C) $NH_4$-saturated bentonite fixed 7 me. per 100 g. after this treatment. These results indicate that this type of treatment should be studied further with bentonite.

Drying the $NH_4$-saturated bentonites, even at 110°C, resulted in a loss of $NH_3$. Presumably H ions were left behind and the bentonite should therefore have become quite acid. To determine if this was the case, 0.5 g. samples of bentonite that had been $NH_4$-saturated and dried at 350°, 110° and 25°C were shaken in 50 ml. of 1 N NaCl for 24 hours, and the pH of the filtrate determined with a glass electrode. The bentonite samples, their drying temperature and the pH values observed are given in table 32.

Table 32. Effect of drying temperature on the pH of NaCl extracts of $NH_4$-saturated bentonites

| Sample | Drying temp. | Extract pH |
|---|---|---|
| 2C | 350°C | 3.1 |
| 2B | 110°C | 4.6 |
| $T_{5a}$ | 25°C | 5.8 |
| NaCl | - | 6.2 |

These results show that the bentonite samples are indeed quite acid after they are $NH_4$-saturated and heated to 350°C. This acid condition could cause some of the lattice Al to be released and it may be that this Al is responsible for the increase in $NH_4$ fixation that is observed with heating. That is, this released Al may be located between the layers of the

contracted lattice and it may be preventing the contracted lattice layers from expanding. If so, part of the fixed $NH_4$ may be simply trapped $NH_4$.

In summary it can be said that the possible effects of this artificial acidity upon the behaviour of the clay, the probability that ammonium complexes and non-ammonium forms of N make up a considerable part of the total nitrogen present after 350°C heating, throw considerable doubt on the practical significance of even the limited amount of fixation exhibited by the heated bentonite.

## REPLACEABILITY OF $NH_4$ IN MICACEOUS MINERALS WITH SOLUTIONS CONTAINING SODIUM TETRAPHENYLBORON

For studies of $NH_4$ release from the principal fixing minerals, vermiculite and illite, the use of a precipitant capable of keeping the solution concentrations of both the cation of interest and the chief interfering cation, K, at low levels, has obvious advantages. Indeed, complete replacement of a fixable cation can only be achieved, apart from the use of methods which destroy the lattice, by keeping the concentrations of all fixable cations essentially zero, since they are, in effect, selectively adsorbed due to lattice contraction following their adsorption. Since sodium tetraphenylboron ($NaBPh_4$) precipitates both $NH_4$ and K in very insoluble form, this compound has great potential for use in the displacement of fixed cations.

A procedure designed to utilize $NaBPh_4$ in removing $NH_4$ from soils would have to include first the replacement of the $NH_4$, then the separation from the soil of the precipitated ammonium without reversion back onto the colloids and without decomposition of organic matter, followed by the quantitative determination of the $NH_4$ extracted. Precipitates of K and $NH_4BPh_4$ can be readily dissolved in acetone-water mixtures or they can be decomposed by heating the aqueous solution to boiling temperature, especially in the presence of $HgCl_2$. Recent work with $NaBPh_4$ by Scott, Hunziker and Reed (1959) and Scott, Hunziker and Hanway (1960) can be given as references for the

preceding statements.

In the experimental work with $NaBPh_4$ as a precipitant, the objectives were to attempt to arrive at a procedure which would give a rapid and accurate measure of the exchangeable $NH_4$ in clays and soils, using more or less neutral salt solutions to extract $NH_4$ in order to minimize decomposition of clay and organic matter. Since distillation of $NH_4$ from alkaline system is by far the simplest method of determining amounts of this cation once extracted, a distillation procedure known to cause little or no decomposition of soluble N-containing compounds in soil is essential. The borate buffer distillation technique adaptable to large volumes of solution and described by Bremner and Shaw (1954), is one of these. Room temperature distillation using MgO as described by Bremner and Shaw (1955) is another specialized method suitable for small volumes of solution or digest, and a short term steam distillation using MgO described on page 44 is unquestionably the best for use with soils. Since no organic matter was present in the vermiculite used on the exploratory work the various distillation techniques were compared to the more usual procedures which employ NaOH as the alkali.

Two major subdivisions can be made of the experimental data on the use of $NaBPh_4$ to extract $NH_4$ from clays. They are first, direct distillations (from alkaline systems) of the $NH_4$ in $NH_4$-saturated clay without prior use of extracting solutions and second, extraction using salts and buffers containing $NaBPh_4$

for varying periods prior to distillation. With respect to the use of $NaBPh_4$ in direct distillations, while it was realized that the $NH_4$ displaced from the clay would be lost as $NH_3$ almost immediately, it was felt that the $NaBPh_4$ might reduce K concentrations and thereby make alkaline distillation even more effective.

The data obtained in various experiments with direct distillation methods are presented in tables 33-37, inclusive. The results of NaOH and borate buffer distillations using 0.25 g. of vermiculite 3B in 300 ml. of the alkaline solutions are contained in table 34. The room temperature distillation results in table 35 were obtained with 10-15 mgm. of clay and 3 to 4 ml. of base. The steam distillations, reported in table 36

Table 33. 1 hour distillations of $NH_3$ from small amounts of $NH_4Cl$ in 300 ml. of solutions with and without added K and $NaBPh_4$

| System | $NH_4$ recovered, % | |
|---|---|---|
| | NaOH | Borate buffer |
| 1. 0.14 me. $NH_4Cl$ | 100.0 | 100.0 |
| 2. 0.14 me. $NH_4Cl$ + $NaBPh_4$ | 100.0 | 100.0 |
| 3. As 2 + 0.14 me. of K | | 99.5 |
| 4. As 2 + 0.28 me. of K | | 99.6 |
| 5. As 2 + 0.42 me. of K | 99.6 | 99.5 |

Table 34. Distillation of 0.25 g. of vermiculite 3B in 300 ml. of solution for 1 hour

| System | $NH_4$ removed, % | |
|---|---|---|
| | 1 N NaOH | Borate buffer |
| 1. Vermic. alone | 97.6 | 94.9 |
| 2. Vermic. + 1 me. KCl, added before base | 70.9 | 12.1 |
| 3. As for 2 + 0.5 me. $NaBPh_4$ | 98.3 | 96.1 |
| 4. As for 2 + 1.5 me. $NaBPh_4$ | 95.2 | 24.4 |
| 5. As for 3, but 200 ml. borate buffer used instead of 50 ml. | - | 95.7 |
| 6. As for 3, but 1 N NaCl used instead of water to dilute 50 ml. borate buffer to 300 ml. | - | 97.8 |

Table 35. Room temperature distillations of $NH_4Cl$ and $NH_4$-saturated vermiculites 2B and 3B using 3-4 ml. of base, for 8 days

| System | $NH_4$ removed, % | | |
|---|---|---|---|
| | 12% MgO susp. | 2 N NaOH | 2 N KOH |
| 1. 100 Mg. $NH_4$ as $NH_4Cl$ | 94.0 | | |
| 2. As 1 + 0.05 me. $NaBPh_4$ | 63.5 | | |
| 3. 15 mgm. 3B vermic. + 0.05 me. $NaBPh_4$ | 62.8 | | |
| | MgO + 2 N NaCl | | |
| 4. 10 mgm. 2B vermic. alone | 95.0 | 99.4 | 1.6 |
| 5. 10 mgm. + 0.2 me. $NaBPh_4$ | 25.6 | 102.6 | 1.0 |
| 6. As for 5 + 0.1 me. KCl | 53.2 | 89.0 | - |

Table 36. Direct steam distillations of 0.1 g. vermiculites 2B or 3B in 40 ml. solution

| Added before distill. | $NH_4$ removed, % Distillation time in minutes 4 | 8 | 12 | 16 |
|---|---|---|---|---|
| 1. 1 N NaOH | 81.3 | 86.2 | 90.1 | 92.1 |
| 2. 1 N NaCl + MgO | 55.9 | 66.3 | 73.3 | 76.2 |
| 3. 20 ml. 1 N NaOAc buffer + $HgCl_2$ + $Na_2S_2O_3$ + NaCl + NaOH, total 40 ml. | 86.8 | 90.4 | 93.4 | - |
| 4. As for 3 but $NaBPh_4$ added in excess of total $NH_4$ + K in vermic. | 84.9 | 88.4 | 90.4 | - |

Table 37. Steam distillations of 0.05 or 0.1 me. of $NH_4$ as $NH_4Cl$

| Added before distill. | $NH_4$ removed, % Distillation time in minutes 4 | 12 |
|---|---|---|
| 1. $H_2O$ + NaOH | 100.0 | - |
| 2. 1 N NaOAc - HOAc buffer + NaOH | 100.0 | - |
| 3. As for 2 + 2 me. $NaBPh_4$ | 100.0 | - |
| 4. As for 3 + 1 me. KCl | 86.6 | 88.2 |
| 5. $H_2O$ + MgO | 100.0 | |
| 6. 1 N NaOAc - HOAc buffer + MgO | No titration - indicator affected | |
| 7. As for 6 + $NaBPh_4$ | No titration - indicator affected | |

were carried out using 0.1 g. of clay and a total of 40 ml. of solution. The amount of $NaBPh_4$ present in each system is not stated in every case, but it was customary to add at least a 3-fold excess of $NaBPh_4$ i.e. 3 times as much as would be required to precipitate all of the $NH_4$ present. Where $HgCl_2$ was added, an amount slightly in excess of that required to precipitate the $NaBPh_4$ present was used. $Na_2S_2O_3$ was always added with $HgCl_2$ to prevent formation of HgO, which can complex $NH_4$. The results are expressed as the percentage of the total $NH_4$ removed since 2 vermiculites (2B and 3B) were used as well as $NH_4Cl$ solutions.

The addition of $NaBPh_4$ by itself did not interfere with the distillation of $NH_4$ in solution, and it did counteract the effect of K added to $NH_4$-saturated vermiculite prior to distilling in NaOH (tables 33 and 34). However, the addition of $NaBPh_4$ did not make a 1 hour NaOH distillation more effective in removing $NH_4$ from vermiculite.

The borate buffer (pH 8.8) was equally as effective as 1 N NaOH in displacing $NH_4$ from vermiculite at the same concentration of Na ions. This was to be expected in view of earlier data on pH vs. $NH_4$ removed from vermiculite. However, neither the NaOH nor the borate buffer distillations removed all of the $NH_4$ from vermiculite in 1 hour with or without added $NaBPh_4$. This is over twice the length of time required to distill $NH_4$ from solution and therefore likely to lead to decomposition of organic matter even at pH 8.8. It is evident from table 36

that the normal steam distillation time of 4 minutes used to remove $NH_4$ from solution was far too short to permit a high percentage recovery of the $NH_4$ in vermiculite.

Studies in the use of $NaBPh_4$ in the removal of K from micas and clays have shown that heating, even to 100°C in solution, is a very good method of decomposing $NH_4$ $BPh_4$ and $KBPh_4$. Therefore it is not surprising that the addition of $NaBPh_4$ immediately prior to direct boiling distillation did not increase the effectiveness of the alkaline solutions.

The boiling and steam distillations would therefore appear to be unsatisfactory due to the high temperature. The room temperature distillations (table 35), using a mixture of NaCl and MgO to displace and distill the $NH_4$ in the vermiculite, likewise proved to be ineffective in the presence of $NaBPh_4$. Since the solubility of $NH_4BPh_4$ is very low at 25°C, any $NH_4$ precipitated in this form would decompose very slowly. The addition of $NaBPh_4$ to room temperature alkaline distillations would therefore slow down the rate of recovery of $NH_4$ if any precipitation took place. A white precipitate of $NH_4BPh_4$ invariably formed on the edges of $NH_4$-saturated clay particles soon after they were placed in a strongly alkaline solution containing $NaBPh_4$.

It is apparent from the results in the preceding section that the $NH_4$ could not be removed from a clay mineral like vermiculite by direct alkaline distillation in a period of contact short enough to avoid decomposition of organic matter.

Also, any advantage to be gained by the use of $NaBPh_4$ to precipitate K and $NH_4$ was lost by using a high temperature distillation. It would therefore seem logical to expect that the $NaBPh_4$ would be more effective if used in an extracting solution at room temperature, providing that all of the precipitated $NH_4BPh_4$ could then be separated from the clay or soil being extracted. Experiments were therefore set up to investigate methods of measuring the amount of $NH_4$ precipitated as $NH_4BPh_4$ following a period of contact between $NH_4$-saturated vermiculite and a buffered salt solution containing $NaBPh_4$.

Equilibrations were carried out with varying amounts (0.1 to 0.5 g.) of vermiculites 2B and 3B in 20 ml. of 1 N NaOAc-HOAc (pH 4.8) or 1 N $NaH_2PO_4$ (pH 6.5), with and without added K and/or $NaBPh_4$ for periods of 1 to 2 days. Distillations were made from solutions made alkaline with borate buffer (pH 8.8), NaOH or KOH. $HgCl_2$ was added in some distillations in an amount in excess of the $NaBPh_4$ present in order to speed up the breakdown of $NH_4BPh_4$. Whenever $HgCl_2$ was added, a few ml. of 1 N $Na_2S_2O_3$ were included to prevent the formation of HgO and the consequent complexing of $NH_3$ under alkaline conditions. The results, and brief descriptions of the equilibration and distillation practices followed, are given in tables 38 and 39.

A comparison of the results of borate buffer distillations of $NH_4$ vermiculite carried out directly vs. after an equilibration in salt solutions (tables 34, 38) showed that there was essentially no difference where the boiling distillation was

Table 38. $NH_4$ recovered from $NH_4$-saturated vermiculite 2B by a 48 hour equilibration in NaOAc-HOAc buffer followed by a 1 hour borate buffer distillation in the presence of the clay

| System | $NH_4$ recovered, % |
|---|---|
| 1. Vermic. + NaOAc-HOAc buffer | 95.0 |
| 2. As for 1 + 0.5 me. $NaBPh_4$ | 80.2 |
| 3. As for 1 + 0.2 me. KCl | 49.3 |
| 4. As for 3 + 0.5 me. $NaBPh_4$ | 87.6 |

Table 39. $NH_4$ recovered from $NH_4$-saturated vermiculite 2B by equilibrating 0.2 g. clay with 20 ml. of various buffer solutions for 24 hours followed by boiling distillation with 1 N KOH or by steam distillation using NaOH, in the presence of the clay

| System | $NH_4$ recovered, % |
|---|---|
| 1. $NaH_2PO_4$ + clay, filtered and filtrate distilled using 1 N KOH | 79.8 |
| 2. $NaH_2PO_4$ + clay + $NaBPh_4$, all distilled directly in 1 N KOH | 7.5 |
| 3. $NaH_2PO_4$ + clay, NaOH steam distilled (3 min.) | 93.4 |
| 4. $NaH_2PO_4$ + clay + $NaBPh_4$ steam distilled (3 min.) with added $HgCl_2$, $Na_2S_2O_3$ | 96.5 |
| 5. As for 4, but $Na_2S_2O_3$ ommitted during distill. | 63.1 |
| 6. NaOAc-HOAc + clay + $NaBPh_4$, NaOH steam distill. (3 min.) with $HgCl_2$, $Na_2S_2O_3$ | 93.4 |
| 7. As for 6, but 2.5 ml. 2 N KCl added before $HgCl_2$ at time of distill. | 89.4 |
| 8. As for 6, but 10 g. KCl salt added prior to distill. | 23.4 |
| 9. As for 6 but 10 ml. 2 N NaCl added prior to distill. | 95.2 |
| 10. As for 6 but 10 ml. $H_2O$ added prior to distill. | 95.4 |

carried on for 1 hour. The addition of KCl to the flasks prior to distillation, even in the presence of $NaBPh_4$, lowered recovery of $NH_4$. It does not seem possible therefore to distill off $NH_4$ from aqueous solutions in the resence of an excess of K to prevent reversion of $NH_4$ back to the clay. It is apparent, too, that $HgCl_2$, added in an amount sufficient to precipitate all of the tetraphenylboron in the mixture, increased the recovery of $NH_4$ in a 3 minute steam distillation, providing that $Na_2S_2O_3$ was also added.

An attempt was made to separate the precipitated K and $NH_4BPh_4$ from the clay by filtering after equilibration, followed by dissolution of the precipitates on the filter paper using hot NaCl solutions containing $HgCl_2$. The yields of $NH_4$ obtained were from 90-94 percent of the total after a 24 hour equilibration of the clay in a NaOAc-HOAc buffer with added $NaBPh_4$. To provide some estimate of the maximum extraction possible in a 24 hour period with a NaOAc buffer without added $NaBPh_4$, 5 successive extractions with fresh 1 N NaOAc solution for periods of 2, 4, 8, 10 hours (total 24 hours) were made of $NH_4$-saturated vermiculite 3B. A total of 81.3 me. out of the 85.8 me. per 100 g. present were extracted, or 94.8 percent. The leaching technique therefore was apparently removing most, if not all, of the $NH_4$ precipitated as $NH_4BPh_4$ during a 24 hour treatment with a NaOAc-$NaBPh_4$ mixture.

In view of the problems associated with the distillation of $NH_4$ from $NH_4BPh_4$ in the presence of $KBPh_4$, the procedures

for destroying the $BPh_4$ ion used in K research already referred to on page 178, were tried. The use of heat to destroy $NH_4BPh_4$ in the presence of an excess of K ions was investigated first. After a 6 day extraction of 0.2 g. of $NH_4$-saturated vermiculite 2B with 20 ml. of NaOAc-HOAc buffer (pH 4.9) the suspension was filtered and the residue taken up in 100 ml. of 1 N KOAc-HOAc buffer at pH 5.1. After refluxing 2 hours to break down the tetraphenylboron present, the digest was filtered, made up to a volume of 300 ml. and distilled using NaOH. The results indicated the recovery of 96.2 percent of the total $NH_4$ present.

The second technique borrowed from the work using $NaBPh_4$ in K studies and tried on an exploratory basis in separating precipitated $NH_4BPh_4$ from clays, was the use of acetone as a solvent. An experiment was conducted to find out whether the $NH_4$ from precipitated $NH_4BPh_4$ could be distilled after dissolution in a mixture of acetone and water. A small amount of $NH_4$ (1 ml. of 0.1 N $NH_4Cl$) was distilled from 30 ml. of $H_2O$ using MgO and a 4 minute steam distillation. The experiment was repeated substituting acetone for 20 of the 30 ml. of $H_2O$. This amount of acetone was added to a similar system after the 0.1 me. of $NH_4$ had been precipitated by the addition of 0.3 me. of $NaBPh_4$, with and without 2 me. K added as KCl after the $NaBPh_4$. The results are given in table 40 as percentage recoveries of the $NH_4$.

The acetone distilled over rapidly (20 ml. in 2 min.) and appeared to carry with it practially all of the $NH_3$. The

Table 40. Recovery of $NH_4$ from precipitated $NH_4BPh_4$ dissolved in acetone and steam distilled using MgO

| System | Recovery, % |
|---|---|
| 1. $NH_4Cl + H_2O + MgO$ | 100.0 |
| 2. $NH_4Cl + H_2O$ + acetone + MgO | 98.7 |
| 3. Same as 2 with $NaBPh_4$ added before acetone | 98.8 |
| 4. Same as 3 with 2 me. K as KCl added after $NaBPh_4$ | 98.9 |

end-point of the methyl red-bromcresol green indicator was sharp in the acetone-boric acid mixture, although the color at the end-point was different in the presence of acetone. The blank determinations for the acetone-water mixtures required a small amount of acid in order to approximate the color, at the end-point, of the distillate collected from the samples containing $NH_4$. The recoveries of $NH_4$ in the presence of acetone appeared to be low by the amount of acid required to titrate the corresponding blanks.

Samples of vermiculite 2B (0.1 g.), illite 2C (0.1 g.) and bentonite 2B (0.2 g.) were equilibrated for varying lengths of time in 10 ml. of 1 N NaCl containing 0.3 me. $NaBPh_4$. The pH of the NaCl-$NaBPh_4$ mixture was adjusted before use to 6.0 using HCl. The equilibrations were carried out in steam distillation flasks (100 ml.) and 2.5 ml. of 1 N KCl, 20 ml. of acetone and MgO (about 1 g.) were added in that order immediately prior to

distilling for 4 minutes. The amounts of $NH_4$ recovered from the 3 clays using this technique are given in table 41. Recoveries are expressed as me. $NH_4$ per 100 g. of oven-dry clay and as percentages of the total present.

Table 41. $NH_4$ recovered from $NH_4$-saturated clays equilibrated in NaCl - $NaBPh_4$, then steam distilled following the addition of acetone

| Samples | Equilibration time (days) | $NH_4$ recovered | |
|---|---|---|---|
| | | me./100 g. | % |
| Vermic. 2B | 1 | 70.1 | 85.4 |
| | 4 | 76.3 | 92.9 |
| | 10 | 74.4 | 91.5 |
| Illite 2C | 1 | 64.2 | 89.7 |
| | 2 | 65.3 | 91.2 |
| | 4 | 65.0 | 90.8 |
| | 6 | 65.0 | 90.8 |
| Bentonite 2C | 1 | 25.2 | 60.7 |
| | 2 | 27.6 | 66.5 |
| | 4 | 26.6 | 64.1 |
| | 6 | 27.5 | 66.3 |

The results with vermiculite were low compared with other techniques and previous $NaBPh_4$ extractions in buffered solutions. It was felt that perhaps precipitation of $NH_4$ as $NH_4BPh_4$ might have occurred during the distillation as the acetone concentration dropped. However, a second addition of acetone following the first distillation gave exactly the same answer for $NH_4$ removed by a 1 day extraction of vermiculite 2C with 1 N NaCl-$NaBPh_4$ (85.4 percent). There is the possibility that an

increase in pH occurred during the equilibration causing some loss of $NH_3$, and the decrease in recovery of $NH_4$ with increased equilibration time after 4 days would suggest that this is what was happening.

The amount of $NH_4$ removed from illite 2C by the NaCl-$NaBPh_4$ mixture was higher than by any other extractant except boiling NaOH. This would suggest that the addition of $NaBPh_4$ to a NaCl solution permits less $NH_4$ to be present in solution than a Na or H-saturated resin. The slight decrease in recovery with time could likewise indicate some loss of $NH_3$.

The bentonite released more of its $NH_4$ to the NaCl-$NaBPh_4$ than to NaCl alone. However, as indicated in the discussion of the results of the bentonite extractions the blocking due to $NH_4$ or K in solution does not appear to be the chief factor limiting the amount of $NH_4$ removed from this clay. Consequently a large increase in recovery of $NH_4$ by 1 N NaCl due to the addition of $NaBPh_4$ could not be expected.

The use of $NaBPh_4$ in neutral, buffered extracting solutions to remove $NH_4$ from soils and clays therefore appears to warrant further study. The use of acetone as a solvent for the $NH_4BPh_4$ followed by a short steam distillation in the presence of MgO to remove the $NH_3$ are the techniques which hold the most promise for bringing about effective separation and measurement, respectively, of the $NH_4$ which has been displaced from a soil or clay and precipitated as $NH_4BPh_4$.

# GENERAL DISCUSSION AND CONCLUSIONS

The objective of this investigation was to compare the replaceability of the $NH_4$ adsorbed on representative di- and trioctahedral clay minerals known to exhibit cation fixation. In order to keep the variables to a minimum in the attempt to get more information on the principles governing the fixation and release of K and $NH_4$ by soil minerals, clays from natural deposits were used. These included a trioctahedral Montana vermiculite containing biotite, samples of dioctahedral Grundite-illite and a Wyoming bentonite consisting largely of finely divided dioctahedral montmorillonite.

It became apparent early in the investigations that the amounts of $NH_4$ adsorbed and retained by the 3 clay minerals could be changed to varying degrees by the methods of preparation used. Since the conditions under which clays capable of fixing $NH_4$ will actually do so are of importance in interpreting the results of fixation studies with soil colloids, considerable time was spent in the preparation of $NH_4$-saturated clay minerals for use in exchange studies.

The natural illite was found to contain over 6 me. of N per 100 g. This native nitrogen was shown to be present partly as inorganic fixed $NH_4$, and partly as organically bound nitrogen. Heating the illite at 450°C for 24 hours completely removed this native nitrogen and also oxidized most of the organic carbon, apparently without adversely affecting the

cation exchange capacity of the material. The small amount of native N in the bentonite was also removed completely by a similar heat treatment. The use of this heating technique to remove organic matter from soil clays would also seem to merit some attention, especially if they are to be used in studies involving the use of inorganic nitrogen-containing compounds.

The removal of most of the interlayer K from the vermiculite-biotite mixture, using a solution containing NaCl and $NaBPh_4$, resulted in an increase of about 100 percent in the amount of $NH_4$ adsorbed by the material, and practically all of the additional $NH_4$ was not replaceable by KCl or KOH. A similar degradation of the Grundite-illite resulted in a total adsorption of $NH_4$ by the illite which was comparable to the amounts of this ion retained by natural vermiculite and bentonite. The natural illite was transformed by the degradation from a material which fixed practically no $NH_4$ to a clay mineral which fixed a large amount of this cation. The amount of native fixed K removed was balanced by a corresponding increase in total $NH_4$, most of which was in turn nonexchangeable to potassium. The natural illite, therefore, was made to behave like some soil illites by simply removing part of the K present. This would substantiate the observation of Allison and Roller (1955) that weathering of soil illites is responsible for their greater exchange capacites and fixing abilities as compared to reference clay minerals. The Wyoming bentonite was found to contain very little K, and the degradation technique as used with illite

and vermiculite removed none of this whatsoever.

Since $NH_4$-saturated vermiculite apparently loses little or no interlayer water and no $NH_3$ when dried at 110°C, as shown by Scott, Hanway and Stanford (1956), drying at this temperature could not be expected to result in lattice collapse and additional $NH_4$ fixation. The amounts of $NH_4$ removed by KCl or KOH from $NH_4$-saturated air-dried vermiculite are low and fixation high, so that no heating is required to produce fixation of interlayer $NH_4$ in this clay. Although the degraded illite fixed a large amount of $NH_4$ when kept moist, the fixation was increased, at the expense of some loss of total $NH_4$, by drying at 110°C. The effect of air drying was not determined, but it is quite possible that high fixation values might have been obtained with the degraded $NH_4$-saturated illite without drying at 110°C. The montmorillonite, on the other hand, if given no pretreatment prior to $NH_4$ saturation, fixed essentially no $NH_4$. There were indications, however, that treatments designed to remove Fe and Al oxides and interlayer Al did increase both the exchange capacity of the bentonite and the amount fixed against extraction by KOH. Reports of $NH_4$ and K fixation by some soil montmorillonites and not by others may have to do with the presence or absence of interlayer ions or substances which interfere with lattice collapse. Various pre-treatments, such as the use of sodium carbonate by Allison and Roller (1955) and the citrate and dithionite treatments used to a limited extent in the current study, should be investigated further in relation to $NH_4$

fixation by bentonite. The drastic 350°C heat treatment shown to cause $NH_4$ fixation in bentonite by Hanway, Scott and Stanford (1957) also produced a very acid clay which appeared to contain nitrogen in some form other than as the $NH_4$ ion.

Comparisons were made of the effectiveness of various salts, resins and hydroxides in removing the $NH_4$ from $NH_4$-saturated samples of vermiculite, illite and bentonite. The chief factor governing the amount of $NH_4$ replaced by a given amount of a displacing cation was the amount of $NH_4$ or K present in solution relative to the amount remaining in the clay. Boiling distillations of $NH_4$-saturated vermiculite and degraded and undegraded illite removed all of the $NH_4$ present in the clays in a relatively short time (1 to 4 hours). However, the same technique was not completely effective with the 350°C heated bentonite. The virtual absence of $NH_4$ in solution during such distillations was shown to be largely responsible for the effectiveness of the method.

Cation exchange resins saturated with Na or H were very effective in removing $NH_4$ from $NH_4$-saturated vermiculite, but were only moderately so with the degraded illite and the bentonite heated to 350°C in the $NH_4$-saturated state. With the relatively coarse vermiculite, the H-saturated resin reached equilibrium more rapidly, and extracted more $NH_4$, than was the case with the strictly Na-saturated cation exchange resin. The presence of some exchangeable H on the predominantly Na-saturated resin produced a marked difference in the speed with which

equilibrium was attained and in the total amount of $NH_4$ removed from vermiculite at the maximum level of extraction. Although more $NH_4$ was removed from the degraded $NH_4$-saturated illite by HR as compared to NaR, the amount removed by HR was far short of the theoretical distribution (99.3 percent of the $NH_4$ in the resin phase) approached by both NaR and HR with vermiculite at a ratio of extracting ion to fixed cation of about 125 to 1. The illite therefore exhibits a higher degree of selective adsorption of $NH_4$ than vermiculite, meaning that smaller amounts of $NH_4$ in solution will equilibrate with larger amounts of $NH_4$ in the clay in the case of illite. That is, the blocking affect of small amounts of $NH_4$ in solution upon further removal of $NH_4$ is greater in equilibrium extractions of illite.

Investigations into the use of neutral and acidified salts and acid as extractants to remove the $NH_4$ present in $NH_4$-saturated clays were most extensive with vermiculite. The fact that sodium salt solutions removed less $NH_4$ from vermiculite than the comparable Na-saturated resin again proved to be the result of accumulation of replaced $NH_4$ in solution in the case of the salt. The use of successive extractions to keep the amount of $NH_4$ in solution from building up improved the recovery of $NH_4$ from vermiculite by NaCl solutions. In mixed systems of resins and salts there was a direct positive relationship between the ratio of soluble to total anions and the amount of $NH_4$ in the solution phase. As the amount of $NH_4$ in solution increased, the total recovery of $NH_4$, on the resin and in solution, decreased.

In the case of the degraded illite, successive extractions with NaCl actually removed more $NH_4$ than a continuous treatment with $NaR_1$, something which never occurred with vermiculite. The inference again was that a portion of the interlayer $NH_4$ in illite was more tightly held than any of the interlayer $NH_4$ in the larger vermiculite particles. Neutral salts at room temperature were very effective with the $NH_4$-saturated bentonite dried at 110°C, and relatively ineffective, when used on the material heated to 350°C.

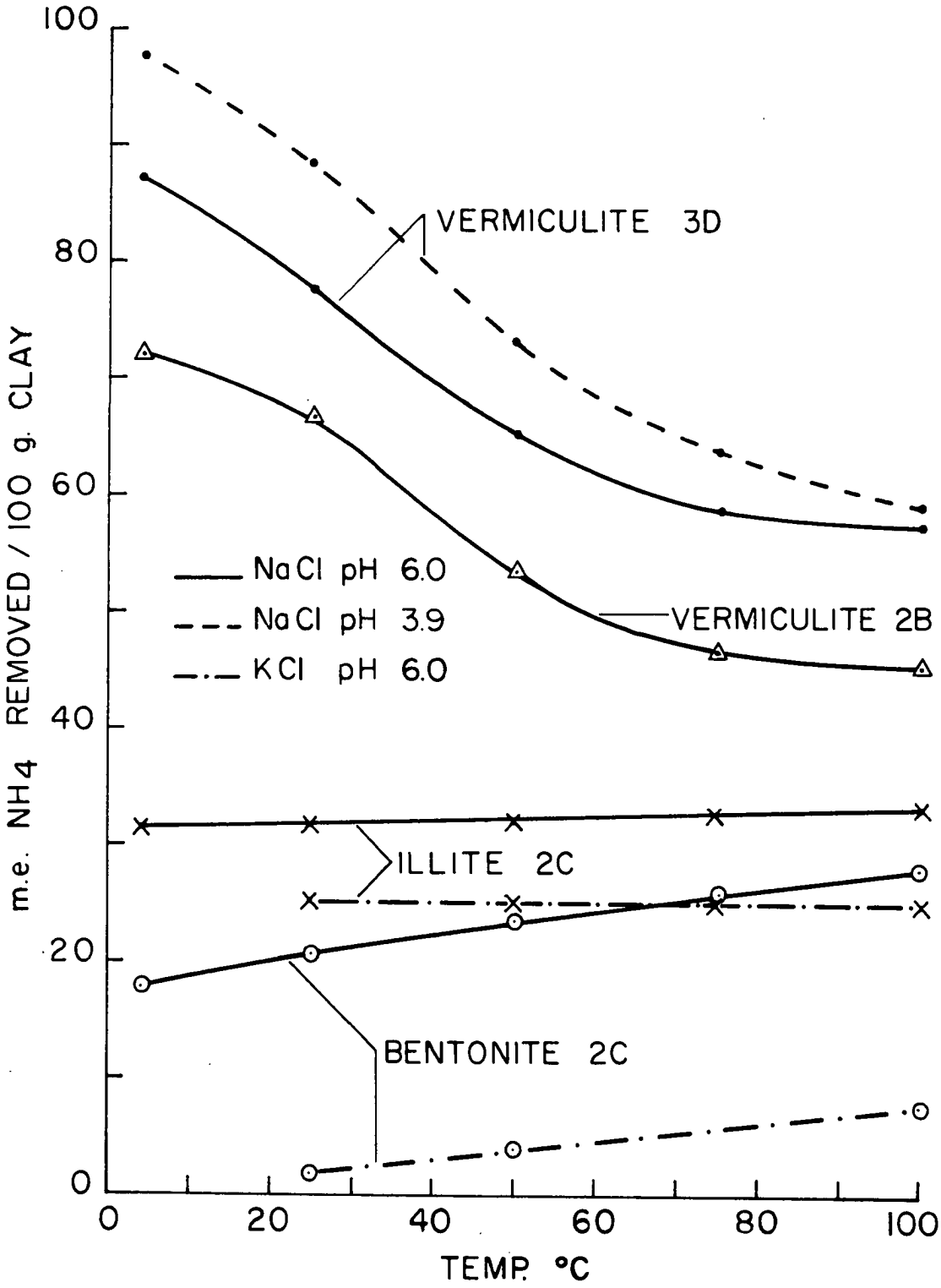
The amounts of $NH_4$ removed by the salt extractions, although primarily determined by the degree of selective adsorption exhibited by the clay, were affected by changes in pH, extraction temperature and the particle size of the clay mineral. The acidity of a salt solution had a pronounced effect on the degree of blocking by displaced $NH_4$ or added K during equilibrium extractions of vermiculite. Under strongly acid conditions, however, the addition of large amounts of K merely slowed down the rate of acid attack on the vermiculite lattice. Illite was relatively unaffected by changes in the pH of the extracting solutions or the amount of H on a Na-saturated resin. In the case of illite, therefore, H was little better as a displacing cation than Na, a marked contrast to the situation with vermiculite. At the other extreme, a high pH was beneficial in extractions of the acid, 350°C heated bentonite due to the fact that the H and/or interlayer Al already present were interfering with exchange of interlayer $NH_4$.

The temperature at which the salt extractions were carried out had a marked effect on the amount of $NH_4$ removed from vermiculite, and the effect was negative. This is in contrast to the lack of temperature effects in the removal of $NH_4$ from illite, and a marked positive effect of temperature on the amount of $NH_4$ removed by both NaCl and KCl from the heated bentonite. In order to illustrate the contrast between the 3 clays with respect to the effect of temperature on the amount of $NH_4$ removed, some of the data already presented have been plotted in figure 19. The amounts of $NH_4$ removed (me. per 100 g.) by comparable salt extractions of vermiculite 2B and 3D, illite 2C and bentonite 2C are given for 4°, 25°, 50°, 75° and 100°C.

The marked difference between the behaviour of illite and vermiculite is not explained by any data available. Since the vermiculite consisted of much coarser material than the illite, the relationship between particle size and extraction temperature should be investigated.

Particle size effects were investigated only with vermiculite. It was demonstrated that grinding this clay to $< 50$ micron size increased the exchange capacity and the amount of $NH_4$ fixed per 100 g. of clay, but decreased the proportion of the total $NH_4$ fixed due to the increase in $NH_4$ on edge exchange sites. The blocking effect of a given amount of K in solutions during NaOH distillation also decreased as particle size decreased. This effect is in contrast to the observed behaviour of the $< 20$ micron illite, since small amounts of K in solution

Figure 19. Effect of temperature on the amounts of $NH_4$ removed from $NH_4$-vermiculites, illite and bentonite by NaCl and KCl.


100
80
60
40
20
0
0
20
40
60
80
100
m.e. NH4 REMOVED / 100 g. CLAY
TEMP. °C
VERMICULITE 3D
VERMICULITE 2B
NaCl pH 6.0
NaCl pH 3.9
KCl pH 6.0
ILLITE 2C
BENTONITE 2C

were very effective in reducing the amount of fixed $NH_4$ displaced from this clay by boiling 1 N NaOH. The difference between illite and vermiculite with respect to the blocking effect of K and $NH_4$ on further $NH_4$ removal therefore is due to causes other than those arising from discrepancies in particle size, although the higher level of exchangeable $NH_4$ in illite appears to be the result of the state of subdivision of this clay.

Finally, limited investigations were made into the use of $NaBPh_4$ as a K and $NH_4$ precipitant, with the ultimate objective of devising a procedure for measuring the total exchangeable $NH_4$ in soils and clays. Although the results of the exploratory studies did not show complete displacement of interlayer $NH_4$ in any of the clays where neutral salt solutions containing $NaBPh_4$ were used as extractants, they were promising enough to warrant continued experimentation.

# LITERATURE CITED

Allison, F.E., Doetsch, J.H. and Roller, E.M. 1953. Ammonium fixation and availability in Harpster clay loam. Soil Sci. 72: 187-200.

Allison, F.E., Kefauver, M. and Roller, E.M. 1953. Ammonium fixation in soils. Soil Sci. Soc. Amer. Proc. 17: 107-110.

Allison, F.E. and Roller, E.M. 1955. Fixation and release of ammonium ions by clay minerals. Soil Sci. 80: 431-441.

Allison, F.E., Roller, E.M. and Doetsch, J.H. 1953. Ammonium fixation and availability in vermiculite. Soil Sci. 75: 173-180.

Amphlett, C.B. 1958. Ion exchange in clay minerals. Endeavour 17: 149-155.

Aomine, S. and Higashi, T. 1953a. Studies on the fixation of ammonium in soils. V. Availability of fixed ammonium by crops. Jour. Sci. Soil and Man., Japan. 23: 105-108.

Aomine, S. and Higashi, T. 1953b. Studies on the fixation of ammonium in soils. VI. Nitrification of fixed ammonium. Jour. Sci. Soil and Man., Japan. 23: 185-188.

Arnold, P.W. 1958. Potassium uptake by cation exchange resins from soils and minerals. Nature 182: 1594-1595.

Attoe, O.J. 1947. Potassium fixation and release in soils occurring under moist and drying conditions. Soil Sci. Soc. Amer. Proc. 11: 145-149.

Barshad, I. 1948. Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analyses, differential thermal curves and water content. Amer. Mineral. 33: 655-678.

Barshad, I. 1950. The effect of interlayer cations on the expansion of the mica type of crystal lattice. Amer. Mineral. 35: 225-238.

Barshad, I. 1951. Cation exchange in soils I. Ammonium fixation and its relation to potassium fixation and to determination of ammonium exchange capacity. Soil Sci. 72: 361-371.

Barshad, I. 1952. Factors affecting interlayer expansion of vermiculite and montmorillonite with organic substances. Soil Sci. Soc. Amer. Proc. 16: 176-182.

Barshad, I. 1954a. Cation exchange in micaceous minerals. I. Replacement of the interlayer cations of vermiculite with ammonium and potassium ions. Soil Sci. 77: 463-472.

Barshad, I. 1954b. Cation exchange in micaceous minerals. II. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite. Soil Sci. 78:57-76.

Barshad, I. 1955. Soil development. In Bear, F.E., ed. Soil chemistry. pp. 1-52. N.Y., Reinhold Publishing Corp.

Bower, C.A. 1950. Fixation of ammonium in difficultly exchangeable form under moist conditions by some soils of semi-arid regions. Soil Sci. 70: 375-382.

Bower, C.A. 1951. Availability of ammonium fixed in difficultly exchangeable form by some soils of semi-arid regions. Soil Sci. Soc. Amer. Proc. 15: 119-122.

Bower, C.A. and Truog, E. 1941. Base exchange capacity determinations as influenced by the nature of the cation employed and formation of basic exchange salts. Soil Sci. Soc. Amer. Proc. 5: 86-89.

Bremner, J.M. 1959. Determination of fixed ammonium in soil. Jour. Agric. Sci. 52: 147-160.

Bremner, J.M. and Harada, T. 1959. Release of ammonium and organic matter from soil by hydrofluoric acid and effect of hydrofluoric acid treatment on the extraction of soil organic matter by neutral and alkaline reagents. Jour. Agric. Sci. 52: 137-146.

Bremner, J.M. and Shaw, K. 1954. Studies on the estimation and decomposition of amino sugars in soil. Jour. Agric. Sci. 44: 152-159.

Bremner, J.M. and Shaw, K. 1955. Determination of ammonia and nitrate in soil. Jour. Agric. Sci. 46: 320-328.

Cornet, I. 1943. Sorption of $NH_3$ on montmorillonite clay. J. Chem. Phys. 11: 217-226.

De Mumbrum, L.E. and Hoover, C.D. 1958. Potassium fixation and release related to illite and vermiculite as single minerals and in mixtures. Soil Sci. Soc. Amer. Proc. 22: 222-225.

Dhariwal, A.P.S. and Stevenson, F.J. 1958. Determination of fixed ammonium in soils. Soil Sci. 86: 343-349.

Dion, H.G. 1944. Iron oxide removal from clays and its influence on base exchange properties and x-ray diffraction patterns of the clays. Soil Sci. 58: 411-424.

Garrels, R.M. and Howard, P. 1959. Reactions of feldspar and mica with water at low temperature and pressure. In Ingerson, Earl, ed. Clays and clay minerals. pp. 133-143. N.Y., Pergamon Press.

Gieseking, J.E. 1939. The mechanism of cation exchange in the montmorillonite-beidellite-montronite type of clay minerals. Soil Sci. 47: 1-13.

Grim, R.E. 1953. Clay mineralogy. N.Y., McGraw-Hill Book Co., Inc.

Grim, R.E. and Bradley, W.F. 1940. Investigations of the effect of heat on the clay minerals illite and montmorillonite. Jour. Am. Ceram. Soc. 23: 242-248.

Gruner, J.W. 1939. Ammonium mica synthesized from vermiculite. Amer. Min. 24: 428-433.

Hanway, J.J. 1954. Fixation and release of ammonium in soils and certain minerals. Unpublished Ph.D. Thesis, Ames, Iowa, Library, Iowa State University of Science and Technology.

Hanway, J.J. and Scott, A.D. 1956. Ammonium fixation and release in certain Iowa soils. Soil Sci. 82: 379-386.

Hanway, J.J. and Scott, A.D. 1957. Soil potassium-moisture relations II. Profile distribution of exchangeable potassium in Iowa soils as influenced by drying and rewetting. Soil Sci. Soc. Amer. Proc. 21: 501-504.

Hanway, J.J., Scott, A.D. and Stanford, G. 1957. Replaceability of ammonium fixed in clay minerals as influenced by ammonium or potassium in the extracting solution. Soil Sci. Soc. Amer. Proc. 21: 29-34.

Hendricks, S.B., Nelson, R.A. and Alexander, L.T. 1940. Hydration mechanism of the clay mineral montmorillonite saturated with various ions. J. Amer. Chem. Soc. 62: 1437-1464.

Jackson, M.L. 1958. Soil chemical analysis. Englewood Cliffs, N.J., Prentice-Hall, Inc.

Jackson, M.L. 1959. Frequency distribution of clay minerals in major Great Soil Groups as related to the factors of soil formation. In Ingerson, Earl, ed., Clays and clay minerals. pp. 133-143. N.Y., Pergamon Press.

Jackson, M.L. and Truog, E. 1940. Influence of grinding soil minerals to near molecular size on their solubility and base exchange properties. Soil Sci. Soc. Amer. Proc. 4: 136-143.

Jansson, S.L. 1958. Tracer studies on nitrogen transformations in soil with special attention to mineralization - immobilization relationships. Kungl. Lantbruks. Annaler 24: 101-361.

Jenny, H. and Overstreet, R. 1939. Cation interchange between plant roots and soil colloids. Soil Sci. 47: 257-272.

Joffe, T.J. and Levine, A.K. 1947. Fixation of potassium in relation to the exchange capacity of soils II. Association fixation of other cations, especially ammonium. Soil Sci. 63: 151-158.

Kardos, L.T. 1955. Soil fixation of plant nutrients. In Bear, F.E., ed. Soil chemistry. pp. 177-199. N.Y., Reinhold Publishing Corp.

Kelley, W.P. 1948. Cation exchange in soils. New York, N.Y., Reinhold Publishing Corp.

Kunin, R. 1958. Ion exchange resins. 2 ed. New York, N.Y., Wiley Press.

Leggett, G.E. 1958. Ammonium fixation in soils and minerals. Unpublished Ph.D. Thesis. Pullman, Wash., Library, State College of Washington.

Mackenzie, R.C. and Milne, A.A. 1953. The effect of grinding on micas. Clay Min. Bull. 2: 57-60.

McBeth, I.G. 1917. Fixation of ammonia in soils. J. Agric. Res. 9: 141-155.

Metson, A.J. 1956. Methods of chemical analysis for soil survey samples. New Zealand Dept. of Sci. and Ind. Research, Soil Bureau, Bul. 12.

Mortland, M.M. and Erickson, A.E. 1956. Surface reactions of clay minerals. Soil Sci. Soc. Amer. Proc. 20: 476-479.

Nommik, H. 1957. Fixation and defixation of ammonium in soils. Acta Agric. Scand. 7: 395-436.

Page, J.B. and Baver, L.D. 1940. Ionic size in relation to fixation of cations by colloidal clay. Soil Sci. Soc. Amer. Proc. 4: 150-155.

Piper, C.S. 1944. Soil and plant analysis. Adelaide, Australia. The Hassell Press.

Pratt, P.E. 1951. Potassium release from Iowa soils by greenhouse and laboratory procedures. Soil Sci. Soc. Amer. Proc. 16: 25-29.

Reitemeier, R.F. 1951. Soil potassium. In Norman, A.G., ed. Advances in agronomy Vol. 3, pp. 113-164. N.Y., Academic Press, Inc.

Rich, C.I. 1960. Aluminum interlayers in vermiculite. Soil Sci. Soc. Amer. Proc. 24: 26-32.

Rodrigues, J. 1954. Fixed ammonia in tropical soils. J. Soil Sci. 51: 264-274.

Salomon, M. and Smith, J.B. 1957. A comparison of methods for determining extractable soil potassium in fertilizer test plots. Soil Sci. Soc. Amer. Proc. 21: 222-225.

Sawhney, B.L. 1958. Aluminum interlayers in soil clay minerals, montmorillonite and vermiculite. Nature 182: 1594-1595.

Schuffelen, A.C. and Marel, H.W. van der. 1955. Potassium fixation in soils. International Potash Institute. Potassium symposium (1955). pp. 157-201.

Scott, A.D., Ahlrichs, J.L. and Stanford, G. 1957. Aluminum effect on potassium fixation by Wyoming bentonite. Soil Sci. 84: 377-387.

Scott, A.D., Edwards, A.P. and Bremner, J.M. 1960. Removal of fixed ammonium from clay mineral by cation exchange resins. Nature 185: 792.

Scott, A.D., Hanway, J.J. and Edwards, A.P. 1958. Replaceability of ammonium in vermiculite with acid solutions. Soil Sci. Soc. Amer. Proc. 22: 388-392.

Scott, A.D., Hanway, J.J. and Stanford, G. 1956. Thermal studies of ammonium fixation and release in certain clay minerals. Amer. Mineral 41: 701-721.

Scott, A.D., Hunziker, R.R. and Hanway, J.J. 1960. Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron I. Preliminary experiments. Soil Sci. Soc. Amer. Proc. 24: 191-194.

Scott, A. D., Hunziker, R. R. and Reed, M. G. 1959. Solubility of potassium tetraphenylboron in acetone-water solutions. Chemist Analyst 48: 11-12.

Ståhlberg, S. 1959. Studies on the release of bases from minerals and soils. I. Release of potassium from potash feldspar and micas at contact with synthetic ion exchangers. Acta Agric. Scand. 9: 361-369.

Stanford, G. 1947. Fixation of potassium in soils under moist conditions and on drying in relation to type of clay mineral. Soil Sci. Soc. Amer. Proc. 12: 167-177.

Stanford, G. and Pierre, W. H. 1946. The relation of potassium fixation to ammonium fixation. Soil Sci. Soc. Amer. Proc. 11: 155-160.

Stevenson, F. J. and Dhariwal, A.P.S. 1959. Distribution of fixed ammonium in soils. Soil Sci. Soc. Amer. Proc. 23: 212-125.

Truog, E. and Jones, R. J. 1938. The fate of soluble potash applied to soils. Ind. Eng. Chem. 30: 882-885.

Volk, N. J. 1934. The fixation of potash in difficultly a available form in soils. Soil Sci. 37: 267-287.

Walker, G. F. 1949a. The decomposition of biotite in soils. Mineralog. Mag. 28: 693-703.

Walker, G. F. 1949b. Water layers in vermiculite. Nature 163: 726.

Walker, G. F. 1950. Vermiculite-organic complexes. Nature 166: 695-697.

Walsh, L. M. and Murdock, J. T. 1960. Native fixed ammonium and fixation of applied ammonium in several Wisconsin soils. Soil Sci. 89: 183-193.

Walsh, T. and Cullinan, S. J. 1945. The effect of wetting and drying on potash fixation in soils. Emp. Jour. Expt. Agric. 13: 203-212.

Wear, J. I. and White, J. L. 1951. Potassium fixation in clay minerals as related to crystal structure. Soil Sci. 71: 1-14.

Welch, L. F. 1958. Availability of nonexchangeable potassium and ammonium to plants and microorganisms. Unpublished Ph.D. Thesis, Ames, Iowa, Library, Iowa State University of Science and Technology.

Welch, L.F. and Scott, A.D. 1959. Nitrification in nutrient solutions with low levels of potassium. Can. Jour. Microbiol. 5: 425-430.

White, J.L. 1951. Transformation of illite into montmorillonite. Soil Sci. Soc. Amer. Proc. 15: 129-133.

Wiklander, L. 1950. Fixation of potassium by clays saturated with different cations. Soil Sci. 69: 261-268.

Wiklander, L. 1955. Cation and anion exchange phenomena. In Bear, F.E., ed. Soil chemistry. pp. 107-148. N.Y., Reinhold Publishing Corp.

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